

SORM, F.

✓ Metabolism of neoplastic tissues. I. Glucose metabolism
in Ehrlich ascites tumor. Libor Šlecht, Alexander Jakš-
bovič, and František Sorm. *Collection Czechoslov. Chem.*
Commun. 20, 803-9 (1955) (in German).—See C.A. 49,
10493d. R. J. C.

(2)

~~FRANTISEK~~
SORM, FRANTISEK

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✓Viruses. IV. Purification of Rous sarcoma virus by differential centrifugation. Libor Šlecht, Alexander Jakubovič, and František Šorm. *Collection Czechoslov. Chem. Commun.* 20, 972-8 (1955) (in English). V. Effect of adenosine, adenylic acid, adenosinetriphosphate, and guanylic acid on the growth of Rous sarcoma. A. Jakubovič, L. Šlecht, and F. Šorm. *Ibid.* 998-1000.—See C.A. 49, 5045d. VI. Effect of 2,4-dinitrophenol upon the biosynthesis of tobacco-mosaic virus. A. Jakubovič and L. Šlecht. *Ibid.* 976-8 (in German).—See C.A. 49, 10440e.
B. J. C.

(5)

Category: Czechoslovakia

B-9

Abs Jour: Zh.-Kh. No 3, 1957. 7546

Author : Rocek, J. and Shorm, F.

Inst : Not given

Title : Oxidation with Chromic Oxide. I. The Oxidation with Chromic Oxide as an Acid-Catalyzed Reaction. (Rocek, J. and Shorm, F.).
II. On the Solubility of Chromic Oxide in Acetic Acid (Rocek, J.)

Orig Pub: Sb. chekhosl. khim. rabot, 1955, Vol 20, No 5, 1009-1017; 1249-1250 (in German with a summary in Russian)

Abstract: No abstract. See RZhKhim, 1956, 46401.

Card : 1/1

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CIA-RDP86-00513R001652420015-5

CZECHOSLOVAKIA/Organic Chemistry. Natural Substances
and Their Synthetic Analogues.

Abs Jour: Ref Zhur - Khimiya, No. 8, 1957, 26968.

Author : Lábler, Ludovík, Černý, Václav, Šorm, František.

Inst :

Title : Steroids. XIX. Proof of Structural Connection
between Holarrhimine and Conessine.

Orig Pub: Sb. chekhosl. khim. rabot, 1955, 20, No. 6,
1484 - 1489; Chem. listy, 1955, 49, No. 9,
1389 - 1394.

Abstract: It was shown by the conversion of dihydrotetra-
methylholarrhimine (I) into derivatives of co-
nessine that holarrhimine (III) has a steroid
skeleton with a 3 β -amino group. This experi-
mentally proved the assumption (see Siddiqui S.,
Pros. Ind. Acad., 1936, A3, 249; RZhKhim, 1954,

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CZECHOSLOVAKIA/Organic Chemistry. Natural Substances E-3
and Their Synthetic Analogues.

Abs Jour: Ref Zhur - Khimiya, No. 8, 1957, 26968

benzene extracts 164 mg of 5,6-dihydroconessimethine (VI), melting point 64 to 65° (from aqu. acetone), and ether extracts 155 mg of dihydroconessine (VII), melting point 107° (from ace-

tone), $[\alpha]_D^{20} + 51.8^\circ$ (c 3.3, in chlorof.). 805 mg of n-toluene sulfonate of monomethyldihydroconessine (VIII), melting point 218 to 221°

(from acetone-CH₃OH), $[\alpha]_D^{20} + 23^\circ$ (c 2.6; in CH₃OH, is obtained after leaving 1 g of I staying in 80 ml of pyridine with 490 mg of n-toluene-sulforchloride for 12 hours, following evaporation in vacuum until dry, neutralization of the aqueous solution of the residue with 500 mg of

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... (washed out with benzene) are obtained from 735 mg of IX by splitting according to Hoffmann and chromatographing with Al₂O₃. The infrared spectra of the obtained substances are attached. See RZhKhim, 1956. 71299 for report.

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CIA-RDP86-00513R001652420015-5

SOIN, F. and KOLTSOVSKY, Vselev

"Amino Acids and Peptides," Chemické Listy, Vol.49, No.2, 1955

Sorm, Frantisek

Reactions of ketene. IV. Reaction with acid chlorides in liquid sulfur dioxide. Jih Smrt, Jih Beránek, and František Sorm (Czech. Akad. věd, Prague). Chem. Listy 49, 78-81 (1955); Collection Czechoslov. Chem. Commun. 20, 285-91 (1955) (in German); cf. C.A. 49, 9545c. Liquid SO_2 proved to be an excellent medium for the reaction of CH_2CO (I) with acid chlorides. The yields of the appropriate acetoacetic derivs. were approx. twice as high as compared to the yields in CHCl_3 . MeNO_2 was less suitable solvent than CHCl_3 , and MeCN gave no yield at all. Reactions were carried out by condensing SO_2 in a flask fitted with a Dry Ice condenser, and by passing I into the liquid SO_2 contg. an acid chloride. EtO_2CCOCl (0.8 g.) in 30 ml. SO_2 was treated during 30 min. with 0.2 mole I, then with 15 ml. abs. EtOH, the mixt. allowed to stand 30 min., and fractionated to give 5.3 g. $\text{EtO}_2\text{CCOCH}_2\text{CO}_2\text{Et}$, b_p 104-10°, n_D^{20} 1.4533. CCl_3COCl (9.1 g.), 30 ml. SO_2 , 0.3 mole I, and 20 ml. EtOH yielded 7.4 g. $\text{CCl}_3\text{COCH}_2\text{CO}_2\text{Et}$, b_p 112-17°. CHCl_2COCl (14.7 g.), 30 ml. SO_2 , 0.4 mole I, and EtOH gave 7.4 g. $\text{CHCl}_2\text{COCH}_2\text{CO}_2\text{Et}$, b_p 115-20°, n_D^{20} 1.4051. Passing 0.2 mole I during 1 hr. into 6.35 g. (COCl_2) in 25 ml. SO_2 , allowing the mixt. to stand 30 min., esterifying with 25 ml. abs. EtOH, evapp. in vacuo, treating the cryst. residue with 5 ml. EtOH, filtering the crystals, and washing them with 3 ml. EtOH yielded 3.7 g. ($\text{COCH}_2\text{CO}_2\text{Et}$) (II), m 81° (from EtOH). Fractionation of the mother liquor gave 2.1 g. $\text{EtO}_2\text{CCOCH}_2\text{CO}_2\text{Et}$, b_p 78-80°, and 1.7 g. II, b_p 110-12°. Total yield of II was 5.4 g. Under the same conditions, I did not react with *meso*-(Br-CHCOCl), b_p 102° (prepd. in 99% yield by treating 16.2 g. fumaryl chloride with 16 g. Br at 40° and irradiation).

V. Reaction of ketene with substituted malonyl chlorides. František Sorm, Jih Beránek, Jih Smrt, and Jih Šícher. Chem. Listy 49, 78-81 (1955); Collection Czechoslov. Chem. Commun. 20, 593-6 (1955) (in German). From many substituted malonyl chlorides tested, only $\text{PhCH}(\text{COCl})_2$ (I), $\text{PhCH}_2\text{CH}(\text{COCl})_2$ (II), $\text{Cl}_2\text{CH}(\text{COCl})_2$ (III) and $\text{CH}_2\text{CH}(\text{COCl})_2$ (IV) react with CH_2CO (V) to give the corresponding dicarboxylates. To prep. I, 10 g. $\text{PhCH}(\text{CO}_2\text{H})_2$ (VI) in 50 ml. Et₂O were treated with 23 g. PCl_5 , the mixt. was refluxed 2-3 hrs., and distd. in vacuo to give 6.8 g. I, b_p 109-10° (method A). I was hydrolyzed to VI, m 151°. Treating 8 g. VI with 18.5 g. PCl_5 , refluxing the mixt. 2 hrs., and distg. it in vacuo yielded 5.7 g. $\text{PhCCl}(\text{COCl})_2$, b_p 83°; $\text{PhCCl}(\text{CO}_2\text{Et})_2$, b_p 144°. $\text{PhCH}_2\text{CH}(\text{CO}_2\text{H})_2$ (35 g.) treated with 59 g. SOCl_2 , heated 2 hrs. at 80°, and distd. in vacuo yielded 23.5 g. II, b_p 110-12° (method B). $\text{PhCH}_2\text{CH}(\text{CO}_2\text{Et})_2$, b_p 125-6°. Refluxing 17.2 g. $\text{CCl}_2(\text{CO}_2\text{H})_2$ and 41 g. PCl_5 2 hrs. on the steam bath yielded 12.8 g. III, b_p 56-7° (method C). The following acid chlorides were prepd. by methods A, B, and C (method

Diri Smrt

% yield, and b.p. given): $\text{MeCH}(\text{COCl})_2$, A, 80, b_p 58°; $\text{Me}_2\text{C}(\text{COCl})_2$, C, 60, b_p 60°; $\text{EtCH}(\text{COCl})_2$, C, 60, b_p 76°; $\text{PrCH}(\text{COCl})_2$, A, 70, b_p 80°; $\text{iso-PrCH}(\text{COCl})_2$, A, 71, b_p 77°; IV, C, 68, b_p 80°; $\text{BuCH}(\text{COCl})_2$, C, 77, b_p 70°; $\text{Bu}_2\text{C}(\text{COCl})_2$, C, 64, b_p 122°. $\text{iso-PrCH}(\text{CO}_2\text{Et})_2$, b_p 114°. $\text{BuCH}(\text{CO}_2\text{Et})_2$, b_p 135°. $\text{Bu}_2\text{C}(\text{CO}_2\text{Et})_2$, b_p 150°. Passing at 0° 0.3 mole V into a soln. of 10.8 g. I in 30 ml. CHCl_3 during 1 hr., and heating the mixt. 20 min. with 20 ml. EtOH gave by distn. 3.3 g. $\text{PhCH}(\text{CO}_2\text{Et})_2$, b_p 74-80°, and 5.5 g. (40%) $\text{PhCH}(\text{CO}_2\text{Et})\text{COCH}_2\text{CO}_2\text{Et}$, b_p 127°, n_D^{20} 1.5074. Similar treatment of 10.5 g. III in 30 ml. CHCl_3 with 0.2 mole and EtOH V gave 7.75 g. $\text{CCl}_3(\text{CO}_2\text{Et})_2$, b_p 110-13°, and 3.25 g. $\text{EtO}_2\text{CCCl}_2\text{COCH}_2\text{CO}_2\text{Et}$, b_p 110-12°, b_p 110°. II (11.55 g.) and 0.4 mole V gave 4.2 g. $\text{EtO}_2\text{CCH}(\text{CH}_2\text{Ph})\text{COCH}_2\text{CO}_2\text{Et}$, b_p 133°, n_D^{20} 1.4983. IV (9 g.) and V gave 0.63 g. $\text{CH}_3\text{CHCH}_2\text{CH}(\text{CO}_2\text{Et})\text{COCH}_2\text{CO}_2\text{Et}$, b_p 95°, n_D^{20} 1.4536.

M. Hudlický

CZECH

1. Proteins. XXX. Inhibition of pancreatic proteases with pancreatic ribonucleic acid. Fraňtíček Štěpán and Miroslava Hrubá (Czech. Acad. Sci., Prague). *Chem. Listy* 49, 115-20 (1955); cf. *ibid.*, 49, 1837. — Polymeric ribonucleic acid prepd. from pancreas inhibits at 25° the protease, esterase, and rennin activity of trypsin, whereas the amidase activity of trypsin and the ability of chymotrypsin to synthesize polypeptides (at optimum pH for the activity) remain intact.

M. Hedický

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CZECH

✓ Mechanism of antibiotic action. VI. Changes in metabolism of *Escherichia coli* accompanying the development of resistance to chloramphenicol. Prantšek Šorm, Dezider Grünberger, and Jan Škoda (Čzech. Acad. Sci., Prague). *Chem. Listy* 49, 121-6 (1955); cf. *C.A.* 49, 4783d.—Two strains of *E. coli* were made resistant to chloramphenicol (I). Changes in the metabolism and morphological properties of I, which accompanied the development of resistance. Slightly resistant strains have lower levels of glutamic acid decarboxylase than the strains of high resistance which have this level almost as high as the strains sensitive to I. With increasing resistance the level of aspartic acid decarboxylase, valine, and leucine (isoleucine); resistant strains do so even in the absence of I.

M. Hudický

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SORM, F.

CZECH

Proteins. XXXI. The active center of trypsin and chymotrypsin. Ivan Rychlík and František Sorm (Česk. akad. věd, Prague). *Chem. Listy* 49, 249-253 (1955); cf. *C.A.* 49, 5541g. —From a study of the literature (Bresler and Rozentsveig, *C.A.* 45, 5204d) and from expts., it follows that the active center of chymotrypsin contains no Mg, and the active center of trypsin contains neither Mg nor Cr. Inhibition of chymotrypsin and trypsin by some complex-forming agents is explained by another mechanism than by formation of complexes with Mg or Cr. M. Hudlický /

~~FRANTISEK~~, JORM, Frantisek

Oxidations with chromium trioxide. I. Oxidation with chromium trioxide as an acid-catalyzed reaction. Jan Roček and Frantisek Šorm (Czech. akad. věd, Prague) *Chem. Listy* 40, 303-305 (1946).—The oxidation of methylcyclohexane (I) with CrO_3 in anhyd. AcOH was studied kinetically under varying concns. of I and in the presence of H_2SO_4 , $\text{CCl}_3\text{CO}_2\text{H}$, H_2O , $\text{Cr}(\text{OAc})_3$, AcONa , and pyridine. The oxidation is strongly catalyzed by strong acids (H_2SO_4 , PhSO_3H) and inhibited by bases such as H_2O , $\text{Cr}(\text{OAc})_3$, and especially by pyridine and AcONa . The inhibition by $\text{Cr}(\text{OAc})_3$ is due to its basicity only, no other specific effect being responsible for the drop of the rate of oxidation. II. Solubility of chromium trioxide in acetic acid. J. Roček. *Ibid.* 369-70.—The soly. of CrO_3 in anhyd. AcOH estd. heretofore as 1% was found to be approx. 0.1% at room temp. The exact detn. of soly. is difficult, since traces of water and of $\text{Cr}(\text{OAc})_3$ increase the soly. considerably. With 99.95% AcOH , 0.1% H_2O doubles the soly. of CrO_3 . 1% H_2O increases the soly. more than 10 times. The $\text{Cr}(\text{OAc})_3$ increase the soly. of CrO_3 ten times as compared with the concn. of H_2O of the same molarity.

M. Hudlický

Syntheses of methylcyclopentenes and proof of their structures. Karel Kochloč, Vladimír Bažant, and František Šorin (Čsl. akad. věd, Prague). *Chem. Listy*, 49, 811 (1955). Pure 1-, 3-, and 4-methylcyclopentenes were prepared, and their structures proved by hydrogenation and oxidation. Their infrared spectra are given. The previous constants for 4-methylcyclopentene (I) (C.A. 29, 5634) were revised. A method has been proposed for v.p.s. the mixt. of methylcyclopentenes obtained as a by-product during catalytic dehydrohalogenation of cyclohexanediol. Adding 50 g. 1-methylcyclopentanediol at 170° to 50 g. molten α -C₁₂H₂₅CO₂H, distg. the mixt., and repeating the process gave 37 g. 1-methylcyclopentene (II), b.p. 74.5-17°, n_D²⁰ 1.4268. Addn. of 16.5 g. II to 100

ml. CCl₄ to 8 g. II in 50 ml. CCl₄ yielded 14.0 g. 1-methyl-1,2-dibromocyclopentane, b.p. 80-4°. Refluxing 1 hr. 11.2 g. cyclopentene in 50 ml. CCl₄ with 20 g. N-bromosuccinimide, filtering off the succinimide, and distg. off the CCl₄ and 4 g. of the unreacted cyclopentene gave 4 g. 3-bromocyclopentene (III), b.p. 34-6°, and 4.3 g. 3,5-dibromocyclopentene, b.p. 81-8°. Adding 4 g. III to a 50-ml. soln. of 0.05 mole MeMgCl in Et₂O, refluxing the mixt. 2 hrs., decomp. with 70 ml. 1:4 HCl, and boiling the product with Na before distn. yielded 1.64 g. 3-methylcyclopentene (IV), b.p. 64°, n_D²⁰ 1.4208. IV and Br gave 73% 3-methyl-1,2-dibromocyclopentane, b.p. 85°. Refluxing 120 g. 4-methyl-3,5-dicarbethoxy-1,2-cyclopentanedione (V) (C.A. 43, 8987e) 5 hrs. with 100 ml. 20% H₂SO₄ and extg. the product with Et₂O gave 30 g. 4-methyl-1,2-cyclopentanedione (VI), b.p. 94.6°, n_D²⁰ 1.4355. 4-methyl-2-ethoxy-2-cyclopentene (VII), b.p. 116°. When 18.2 g. V was refluxed with 100 ml. 20% H₂SO₄, 10% of VI and 12.1% of VII were obtained, resp. VII was also prepd. in a 37% yield by refluxing 6 hrs. 1.3 g. VI with 16.2 g. 20% H₂SO₄ and 1.3 ml. EtOH. Hydrogenation of 28.2 g. VI in 1 l. EtOH over Pt at normal conditions gave 27.3 g. (93%) 4-methyl-1,2-cyclopentanediol (VIII), b.p. 107.8°. Adding 18 g. VIII and 0.8 g. C₆H₅N with ice-cooling to 12 ml. PBr₃ in 7.2 ml. C₆H₆, stirring the mixt. 3 hrs. in an ice bath, 24 hrs. at room temp., and 5 hrs. on a steam bath, de-

compos. the mixt. with H₂O, and extg. with Et₂O yielded 19 g. 4-methyl-1,2-dibromocyclopentane (IX), b.p. 70-80°. Hydrogenation of 19 g. VII over Pt gave 4.45 g. 4-methyl-2-ethoxycyclopentanol (X), b.p. 73-4°, b₁₀₀ 178°. Adding 4.8 g. X to 0.5 g. PBr₃, 0.5 g. C₆H₅N, and 1.7 ml. C₆H₆ with ice-cooling, stirring the mixt. 2 hrs. with cooling and 24 hrs. at room temp., decomp. with 20 ml. ice water, and extg. with Et₂O gave 2.5 g. 4-methyl-2-ethoxy-1-bromocyclopentene (XI), b.p. 86-11°, b₁₀₀ 178°. Refluxing 3 hrs. 9 g. IX with 5 g. Zn shavings in 20 ml. anhyd. PrOH, distg. the product over a column, washing it several times with H₂O, adding 20 ml. xylene, and distg. gave 2.2 g. I, b.p. 69.5°, n_D²⁰ 1.4270. The same product, b.p. 65.66°, n_D²⁰ 1.4296, was obtained in 50% yield by refluxing 19 hrs. 2.07 g. XI with 4 g. Zn in 5 ml. PrOH. Treating 117 mg. IV and 3 ml. 90% HCO₂H with 0.35 ml. 30% H₂O₂, stirring the mixt. 1 hr., while heating to 60°, distg. off the HCO₂H in vacuo, neutralizing the residue with 0.5N NaOH, and extg. with AcOEt gave 103 mg. 3-methyl-1,2-cyclopentanediol. This heated 8 hrs. at 50° with 3 ml. AcOH, 0.5 ml. CHCl₃, and 0.5 g. Pb(OAc)₂ gave after dilg. with 10 ml. H₂O and extg. with Et₂O, CHOCHMeCH₂CH₂CHO the oxidation of which with KMnO₄ yielded 30 mg. HO₂CCHMeCH₂CH₂CO₂H; p-bromophenacyl ester, m. 66°. Similar procedure with I gave 57.5% VIII, and 33.4% HO₂CCH₂CHMeCH₂CO₂H; p-bromophenacyl ester, m. 116.5-17°. Hydrogenation of I, II, and IV over Pt gave methylcyclopentane, m.p. 1.135-1.4137. M. Hudlický.

Sorm, F

6200

Metabolism of neoplastic tissues. 1. Glucose metabolism in Ehrlich ascites tumor. Libor Šlechta, Alexander Jakubovič, and František Sorm (Čsl. akad. věd, Prague). *Chem. Listy* 49: 800-804 (1955). Attempts were made to elucidate the so-called reversed Pasteur effect in the cells of the Ehrlich ascites tumor. From manometric measurements and chem. analyses it follows that the endogenous substrate of these cells is fat. Ascites cells contain no glycogen. Exogenous glucose as a substrate is advantageous as proved by thermodynamic calcs. even if, in the presence of this source of energy, respiration of the ascites cells is inhibited by 50% (av.). M. Hudlický

Sorn, F.

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Reactions of ketene. VI. Reactions with halogen derivatives of sulfur. F. Sorn, J. Smrt, and J. Beránek. (Czech. Akad. věd. ~~Práce~~ Chem. Listy 49, 573-4; Collection Czechoslov. Chem. Commun. 20, 721-3 (1955) (in German); cf. C.A. 49, 15773d. --EtSCl, S₂Cl₂, and SOCl₂ add normally to CH₂:CO (I). SO₂Cl₂ transforms I to ClCH₂COCl, and SCl₂ gives polymers. Passing I (0.6 mole) during 2 hrs. into a boiling soln. of 11.89 g. SOCl₂ in 30 ml. liquid SO₂, adding 25 ml. abs. MeOH, and distg. the mixt. yielded 9.05 g. SO(CH₂CO₂Me)₂, b_p 92°, n_D²⁰ 1.4375. Passing, at -70°, 0.2 mole I during 30 min. into a soln. of 13.5 g. S₂Cl₂ in 25 ml. CHCl₃, adding to the mixt. 25 ml. MeOH, refluxing the mixt. 10 min., and distg. *in vacuo* gave 12.2 g. S₂(CH₂CO₂Me)₂, b_p 103°, n_D²⁰ 1.5163. Passing 30 min. 0.2 mole I into a soln. of 4.5 g. EtSCl in 20 ml. liq. SO₂, and esterifying the mixt. with 15 ml. EtOH gave 4.05 g. EtSCH₂CO₂Et, b_p 73°. M. Hudlický

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SORM, F.

Tenth anniversary of the liberation of our country. p. 629.

CHEMICKÉ LISTY (Ceskoslovenská akademie věd. Československá společnost chemiků) Praha, Czechoslovakia. Vol. 49, no. 5, May 1955

Monthly List of East European Accessions (EEAI) ^{no. 1, Jan} IC, Vol. 9/1960

Sorm, Frantisek

CH

Steroids. XVI. Synthesis and configuration of the two stereoisomeric 3 β ,16-dihydroxyandrostanes. Jan Fajka and Frantisek Sorm (Czech. Akad. v \acute{e} l. Prague). *Chem. Listy* 49, 725-30 (1955); *Collection Czechoslov. Chem. Commun.* 20, 1404-72 (1955) (in English). cf. C.A. 49, 14787A. Catalytic hydrogenation of 3 β ,16 α -diacetoxy-17-oxoandrostane (I) gave 3 β ,16 α -diacetoxy-17 β -hydroxyandrostane (II) which was transformed to 3 β ,16 α -diacetoxy-17 α -bromoandrostane (III) whose catalytic reduction and sapon. yielded 3 β ,16 α -dihydroxyandrostane (IV). Direct transformation of I to IV by way of the Raney Ni desulfurization of 3 β ,16 α -diacetoxy-17-oxoandrostane ethylene mercaptide (V) was unsuccessful since V gave 3 β -acetoxyandrostane (VI). The stereoisomer of IV, 3 β ,16 β -dihydroxyandrostane (VII) was prepd. by reductive cleavage of 3 β -hydroxy-10 β ,17 β -epoxyandrostane (VIII), or by hydrogenation and sapon. of 3 β -acetoxy-10-oxoandrostane (IX). Hydrogenation of 2 g. I in 40 ml. AcOH over Pt, diln. of the mixt. with H₂O, extn. with ether, evapn. of the ext., and crystn. of the residue from Me₂CO yielded 1.2 g. II, m. 188-9°, [α]_D²⁵ +22.3°. Oxidation of 100 mg. II in 2 ml. AcOH with 30 mg. CrO₃ in the min. amt. of H₂O gave 60 mg. I, m. 182-3°, [α]_D²⁵ 54°. II (100 mg.) with Ac₂O in C₁₂H₂₂N gave 90 mg. 3 β ,16 α ,17 β -triacetoxandrostane, m. 170-1° (from EtOH).

[α]_D²⁵ -50°. Refluxing 620 mg. II (dried by distn. with C₆H₆) in 30 ml. C₁₂H₂₂ 29 min. with triphenyl phosphite dibromide (Coc, et al. C.A. 161f), dilg. the cooled mixt. with Et₂O, washing with aq. NaHCO₃ and H₂O, drying the ext., evapn. the solvent, and chromatographing the residue from petr. 3:1 ether-benzene gave 280 mg. III, m. 130-5°, crystals, and melting again at 153-4° (from EtOH). [α]_D²⁵ 17°. Refluxing 200 mg. III with 200 mg. KOH in 20 ml. MeOH 48 hrs., evapn. the MeOH, and extg. the residue with Et₂O gave 80 mg. (60%) 3 β -hydroxy-16-oxoandrostane, m. 156-7° (from MeOH), [α]_D²⁵ -188°. Hydrogenation of 200 mg. III in 15 ml. EtOH over 200 mg. 5% Pd-CaCO₃ (2 addnl. 200 mg. portions of catalyst were added during the hydrogenation; total time 18 hrs.) gave a product m. 172-4° (from EtOH). Since the pure product still contained Br, it was sapon. with KOH in MeOH to a mixt. of 3 β -hydroxy-16-oxoandrostane (X) and IV. The mixt. acetylated and treated with Girard reagent yielded 126 mg. 3 β ,16 α -diacetoxandrostane (XI), m. 170-7° (from EtOH), [α]_D²⁵ -35.8°. Sapon. of X with aq. ethanolic K₂CO₃ gave 78% IV, m. 192-3° (from AcOEt, and by sublimation), [α]_D²⁵ -11°. Benzoylation of IV in pyrrolidine gave 77% 3 β ,16 α -dibenzoyloxyandrostane, m. 183-5°, [α]_D²⁵ 8.8°. Treating 150 mg. X in 4 ml. AcOH with 50 mg. CrO₃ in min. amt. H₂O 24 hrs. at room temp., adding MeOH, H₂O, and extg. the mixt. with Et₂O gave 123 mg. 3,16-dihydroxyandrostane (XII), m. 158-9° (from ligroine), [α]_D²⁵ -162°. XII was also obtained by a similar procedure from IV and from VII, its [α]_D²⁵ being -169° and -165°, resp. Treating 800 mg. I in 4 ml. dioxane with 2 ml. (CH₃SH)₂ and 1 g. anhyd. Na₂SO₄ at 0° 1.5 hrs. with dry HCl, neutralizing the mixt. with anhyd. K₂CO₃, dilg. with Et₂O, removing the excess (CH₃SH)₂ with 5% NaOH, and evapn. the

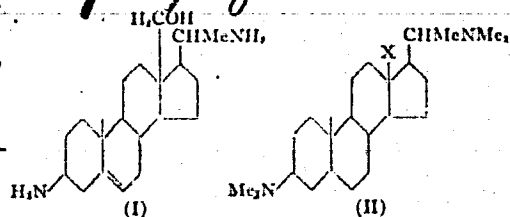
OVER (3)

JAN FAJKOS

Et₂O yielded 620 mg. V, m. 118-19° (from EtOH or Me₂CO contg. pyridine), $[\alpha]_D^{25} -70^\circ$. Refluxing 300 mg. V in 30 ml. dioxane 5 hrs. with 4 g. Raney Ni, removing the catalyst, evapng. the soln., dissolving the oily residue in petr. ether, and applying chromatography gave 90 mg. VI, m. 80-90° (from EtOH), $[\alpha]_D^{25} -8.0^\circ$. Heating 650 mg. VIII in 40 ml. dioxane with 200 mg. LiAlH₄, 15 hrs. at 80° and crystn. from MeOH and C₆H₆ gave 30 mg. 3 β ,17 β -dihydroxy-androstane, and benzoylation of the residue yielded after chromatography 55 mg. 3 β ,16 β -dibenzoyloxyandrostane (XIII), m. 191-2° (from EtOH), $[\alpha]_D^{25} -14^\circ$, and 85 mg. 3 β ,17 β -dibenzoyloxyandrostane, m. 194-5° (from EtOH). XIII was also obtained by benzoylation of VII in 60% yield ($[\alpha]_D^{25} -10^\circ$). Hydrogenation of 500 mg. IX in 10 ml. AcOH over 200 mg. PtO₂, diln. with Et₂O, evapn., and acetylation of the residue with Ac₂O in pyridine gave 400 mg. 3 β ,16 β -diacetoxyandrostane (XIV), m. 107-8°, $[\alpha]_D^{25} -8.5^\circ$. Refluxing 540 mg. XIV in 15 ml. EtOH with 400 mg. K₂CO₃ in 3 ml. H₂O 2 hrs., distg. off the EtOH, and extg. the residue with AcOEt gave 310 mg. VII, m. 180-1° (from AcOEt), $[\alpha]_D^{25} -5.7^\circ$. Hydrogenation of 650 mg. 3 β -methoxy-16-oxo-17 β -acetoxy-5-androstene in 15 ml. AcOEt and 10 ml. EtOH over 10 g. Raney Ni gave 380 mg. 3 β -methoxy-16 β -hydroxy-17 β -acetoxy-5-androstene (XV), m. 126-7° (from MeOH), $[\alpha]_D^{25} -38.5^\circ$. Refluxing 300 mg. XV in 15 ml. MeOH with 300 mg. F₂CO₂ in 2 ml. H₂O 2 hrs.,

distg. off the MeOH, and extg. the residue with AcOEt-Et₂O mixt. gave 210 mg. 3 β -methoxy-16 β ,17 β -dihydroxy-5-androstene (XVI), m. 183-4°, $[\alpha]_D^{25} -65.5^\circ$. Benzoylation of 700 mg. XV in pyridine gave 700 mg. 3 β -methoxy-16 β -benzoyloxy-17 β -acetoxy-5-androstene (XVII), m. 129-30° (from MeOH and ligroine), $[\alpha]_D^{25} 15.4^\circ$. Similar treatment of XV with hexahydrobenzoyl chloride yielded 60% 3 β -methoxy-16 β -hexahydrobenzoyloxy-17 β -acetoxy-5-androstene, m. 144-5° (from MeOH), $[\alpha]_D^{25} -20.2^\circ$. Treating 100 mg. dry XVI with 10 ml. 1.5% HCl in acetone 30 min. at room temp. and neutralizing the mixt. with 2% NaHCO₃ gave 90 mg. (80%) of the acetone of 3 β -methoxy-16 β ,17 β -dihydroxy-5-androstene, m. 140-7°, $[\alpha]_D^{25} -29.2^\circ$. Hydrogenation of XV in AcOH over PtO₂ gave 60% 3 β -methoxy-16 β -hydroxy-17 β -acetoxyandrostane (XVIII), m. 102-4°, $[\alpha]_D^{25} +27^\circ$. Similar hydrogenation of XVII yielded 35% 3 β -methoxy-16 β -hexahydrobenzoyloxy-17 β -acetoxyandrostane, m. 119-20°. Hydrogenation of 100 mg. XVI in AcOH over PtO₂ gave 60 mg. 3 β -methoxy-16 β ,17 β -dihydroxyandrostane, m. 187-8°. Adding 230 mg. dry XVIII in 1.5 ml. CHCl₃ contg. 0.03 ml. pyridine to 0.03 ml. PBr₃ in 2 ml. CHCl₃ during 10 min. at -18°, allowing the mixt. to stand 24 hrs. at room temp., dilg. with Et₂O, washing with NaHCO₃ and H₂O, and evapng. the ext. gave 3 β -methoxy 16 α -bromo-17 β -acetoxyandrostane, m. 109-10°, $[\alpha]_D^{25} -41^\circ$. XVII. The nature of the hydroxyl group in holatrhinine. Václav Černý and František Šorm. *Ibid.* 909-12. — On the basis of oxidation to an aldehyde and acid, and on the basis of the behavior of its Me ester during sapon and LiAlH₄ reduction, structure I has been ascribed to holatrhinine. II (X =

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CH₂OH) (IIa) (1 g.), m. 209-10°, [α]_D²⁰ 10°, in 40 ml. AcOH and 30 ml. H₂O, was oxidized with 400 mg. CrO₃ in 10 ml. H₂O at 17°. After the addn. of 15 ml. MeOH (after 15 hrs.), the mixt. was poured on ice and NH₄OH, the product extd. with Et₂O, the ext. washed with H₂O, dried with MgSO₄, evapd., the partly cryst. residue dissolved in petr. ether, the undissolved portion (35 mg. recovered IIa) filtered off, and the filtrate chromatographed to give 545 mg. II (X = CHO) (IIb), m. 101-3° (from petr. ether), [α]_D²⁵ 55°; oxime, m. 258-60°. Reduction of 145 mg. IIb with 80 mg. LiAlH₄ in 10 ml. Et₂O, alkalization of the mixt. with 50 ml. 15% KOH, and extn. with Et₂O gave 128 mg. IIa, m. 213-14°, [α]_D²⁵ 9.5°. A more efficient oxidation of IIa (1 g.) in 89 ml. AcOH and 11 ml. H₂O with 10 ml. of a soln.

prepd. from 5.3 g. CrO₃, 8 ml. H₂SO₄, and 40 ml. H₂O, destruction of the excess CrO₃ with Na₂SO₃, partial neutralization of the mixt. with a soln. of 3 g. NaOH, three-fold evapn. to dryness *in vacuo* after the addn. of 20 ml. HCl, dissolution of the residue in 30 ml. H₂O, addn. of 100 ml. EtOH, evapn. of the EtOH ext., and purification of the residue from Cr(III) salts gave II (X = CO₂H) (IIc), which was esterified with CH₃N₃ to its *Me* ester (IId) (423 mg.), m. 116-17°, [α]_D³⁰ 30° (from Me₂CO). Sapon. of 34.5 mg. IId by refluxing 4 hrs. with 2.8 ml. EtOH and 0.7 ml. aq. 0.8N NaOH was unsuccessful, and 87% IId was recovered. Reduction of IId with LiAlH₄ in boiling Et₂O (2 hrs.) gave traces of IIa; in boiling tetrahydrofuran (100 mg. IId, 100 mg. LiAlH₄), only 30% IIa was obtained. Infrared spectrum of IIb has a max. at 1715 cm.⁻¹

M. Hudlický

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✓ Amino acids and peptides. XVI. Peptides of DL- α , β -diaminopropionic acid. Karel Paduska, Josef Rüdinger, and František Sorm (Czech. Akad. věd, Prague). Chem. Listy 49, 487-491, Collection Czechoslav. Chem. Commun. 20, 1174-82 (1955) (in English); cf. C.A. 50, 1593k.
 Preps. of DL- α , β -diaminopropionamide (I), DL- α , β -diaminopropionylglycine (II), DL- α , β -diaminopropionylglycinamide (III), N²-glycyl-DL- α , β -diaminopropionic acid (IV), N²-glycyl-DL- α , β -diaminopropionic acid (V), bis-glycyl-DL- α , β -diaminopropionic acid (VI), and of the derivs. are described. Heating 40 g. BrCH₂CHBrCO₂H with 400 ml. aq. NH₄OH, satd. at 0° 3-4 hrs. at 100° in an autoclave, distg. off the NH₃, and treating the soln. with activated C, and filtering gave 14.5-17.5 g. DL-H₂NCH₂CH(NH₂)CO₂H, decomp. 230-2°. N²-carbobenzoyloxy-DL- α , β -diaminopropionic acid, decomp. 234-5°, yield 15%. N²-benzoyl-N²-carbobenzoyloxy-DL- α , β -diaminopropionic acid m. 150-1°. Treating 5.4 g. dicarbobenzoyloxy-DL- α , β -diaminopropionic acid (VII) in 60 ml. dry CHCl₃ at 0° with 3.8 g. PCl₅ until the PCl₅ dissolved, evapg. the mixt. in vacuo at 40°, and extg. the residue with petr. ether gave 3.54 g. DL-4-(carbobenzoyloxymethyl)oxazolidine-2,5-dione (VIII), decomp. 130-40° (from AcOEt-petr. ether). Shaking 1.61 g. VIII at 20° with 30 ml. abs. MeOH contg. 10 millimoles HCl, letting stand 12 hrs., distg. off the MeOH, and crystg. the residue from MeOH-Et₂O mixt. gave 1.60 g. of the HCl salt of Me N²-carbobenzoyloxy-DL- α , β -diaminopropionate, m. 137-8°. In the same way was prepd. 85% HCl salt of Et N²-carbobenzoyloxy-DL- α , β -diaminopropionate (IX), m. 143-4.5°. Treating 1.12 g. VII with 20 ml. N HCl in EtOH overnight gave 1.1 g. Et

dicarbobenzoyloxy-DL- α , β -diaminopropionate, m. 80-91° (from AcOEt-petr. ether); amide, by treatment with MeOH and satd. AcOH, m. 172-3° (from 30% AcOH). with NH₃ in 81% yield, m. 172-3° (from 30% AcOH). Hydrolysis of the amide (0.73 g.) with 10 ml. 37% HBr in Et₂O gave after 1 hr. at 0° 0.51 g. di-HBr salt of I, decomp. 243°. The Et ester (IXa) of di(carbobenzoyloxy)-DL- α , β -diaminopropionylglycine (X) was prepd. in 2 ways: Refluxing 1.97 g. VII in 10 ml. PhMe 2 hrs. with 0.72 g. OCNCHEt₃, distg. off the solvent in vacuo, triturating the residue with satd. soln. of NaHCO₃, and washing the crystals with H₂O, N HCl and H₂O gave 2.2 g. IXa, m. 141-1.5° (from 80% EtOH). Treating 3 g. VII in 20 ml. CHCl₃ at 6° with 0.93 g. 1-EtC₄H₉N and 1.12 sec-BuO₃CCl, adding a cool (-5°) soln. of 0.87 g. H₂NCH₂CO₂Et in 10 ml. CHCl₃, letting the mixt. stand 2 hrs. at -5° and 12 hrs. at room temp., evapg. the solvent, and treating the residue with NaHCO₃ gave 84% IXa. IXa (3.33 g.), 8 ml. N NaOH, 6 ml. MeOH, and 10 ml. dioxane shaken 1.5 hrs., acidified to Congo red with dil. HCl, and the cryst. residue (2.91 g.) treated with HBr in AcOH, the base liberated by means of an ion exchanger, and treated with picric acid to give picrate of II, m. 210° (from H₂O). Satg. 1.5 g. of the Et ester of X in 30 ml. MeOH with NH₃ at 0°, keeping the

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mixt. overnight, distg. off the MeOH, and repeating the procedure with the residue gave 1.18 g. of the amide of X, m. 178-9.5° (from aq. EtOH). Treatment of 0.8 g. of this compd. with HBr in AcOH, with Amberlite, and with picric acid gave 0.76 g. of the dipicrate of III, m. 100-1° (from aq. EtOH). IX (from 2.12 g. IX.HCl and NH₃ in CHCl₃) treated with 1.64 g. PhCH₂O₂CNHCH₂CON₂ gave Et ester of *N*⁸-carbobenzoyloxy-*N*⁹-carbobenzoyloxyglycyl-DL-α,β-diaminopropionic acid (XI) as a gel; the Me ester was prepd. similarly. Sapon. of the Et or Me ester of XI by keeping 1.5 hrs. with *N* alc. NaOH gave 1.58 g. free XI, m. 120-2°.

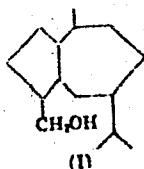
Treatment of XI with HBr in AcOH, filtering the soln. through Amberlite, evapg. the soln. to 10 ml., and adding to 4 ml. 0.23 g. picric acid in 3 ml. EtOH pptd. 0.3 g. of the picrate of IV, decomp. 208° (from H₂O). Dissolving 24 g. of the HBr salt of H NCH₂CH(Sh)₂CO₂H in 130 ml. 2*N* NaOH, cooling the soln. to 0°, and treating during 35 min. with 35 g. tosylglycine chloride in Et₂O and with 300 ml. *N* NaOH, stirring the mixt. 35 min. at 0°, sepg. the aq. layer, extg. it twice with Et₂O, acidifying with HCl to Congo red, reppptg. the sepd. crystals 3 times, and crystg. the prod-

uct from dil. AcOH gave 7.12 g. dihydrate of *N*⁸,*N*⁹-bis-(tosylglycyl)-DL-α,β-diaminopropionic acid (XII), m. 80-2°. Adjusting the pH of the mother liquors to 7 and letting the soln. stand several hrs. at 0° gave 10.67 g., and by evapg. an addnl. 1.84 g. *N*⁸-tosylglycyl-DL-α,β-diaminopropionic acid (XIII), decomp. 202°. Heating 2.77 g. XIII, 2.6 g. PhOH, and 44 ml. 37% HBr in AcOH 2 hrs. at 70° in a pressure bottle, cooling the mixt., pouring it into 150 ml. Et₂O, allowing to stand 2 hrs. in the icebox, washing the crystals several times with Et₂O, dissolving them in H₂O, removing the Br ions with Amberlite in an acetate cycle, evapg. the filtrate *in vacuo*, and treating the residue with 30 ml. EtOH contg. 15 millimoles HCl pptd. an oil which crystd. on trituration at 50°. Dissolving the HCl salt in a min. amt. of H₂O, treating the soln. with 20 ml. EtOH contg. 5 millimoles HCl, and adding Et₂O pptd. 1.45 g. of the HCl salt of V, decomp. 210°. The same product was obtained from XIII in 48% yield by reduction with Na in NH₃. Heating 0.53 g. XII (dried *in vacuo* over P₂O₅), 0.6 g. PhOH, and 10 ml. 36% HBr in AcOH 4 hrs. at 65°, and working up the mixt. as described above yielded 87% of the amino acid and, after adding picric acid, 76% of the picrate of VI, m. 204-5° (decompn.) (from H₂O). Adding at 0° 1 g. tosylglycine chloride in Et₂O soln. to 0.91 g. HCl of the salt of Et *N*⁸-carbobenzoyloxydiaminopropionate in 6 ml. *N* NaOH, shaking the mixt. 1.5 hrs. at 0°, sepg. the aq. layer, extg. it twice with Et₂O, and acidifying with HCl gave an oil which crystd. in the icebox. Repptn. and recrystn. gave 0.29 g. *N*⁸-carbobenzoyloxy-*N*⁹-tosyloxy-DL-α,β-diaminopropionic acid, m. 161-3°. Shaking 0.95 g. XIII, 0.68 g. PhCH₂O₂CCl, and 10 ml. *N* NaOH 2 hrs. at 0°, extg. the soln. twice with Et₂O, and acidifying it with HCl gave an oil which crystd.; after repptn. and recrystn. from aq. EtOH, it m. 155-6° (yield 0.2 g.).

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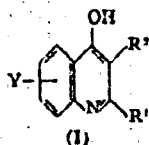
The nature of azulenogenic compounds from *Lactarius deliciosus*. Preliminary communication. V. Benešová, V. Herout, and P. Šotm (Czech. Akad. věd, Prague). *Chem. Listy* 49, 778-80 (1955).--*Lactarius deliciosus* L. contains originally only orange prazulenes, one of which (I) has primary OH group and gualane skeleton, and probably 4-5 double bonds. The other two orange compds. isolated by chromatography are an aldehyde having fewer double bonds than lactaroviolin, and a hydrocarbon contg. fewer double bonds than lactarazulene. Infrared spectra of I and of the product obtained by catalytic hydrogenation of lactaroviolin are given. Also in *Collection Czechoslov. Chem. Commun.* 20, No 2, 510-11 (1955) (in English).



M. Hudcok

SORM, FRANTISEK

Syntheses of 4-hydroxyquinoline derivatives. Frantisek Sorm and Ladislav Novotny (Czech. Akad. Ved, Prague). *Chem. Listy* 49, 801-2 (1955).—As nitrogen analogs of spigelin, a series of quinolines (I), where R¹ and R² are alkyl or aryl groups, and Y one or more OH or alkoxy groups, were prepd. and tested for their spasmolytic effect



which was found with some of them. Essentially 3 methods were used for the prepn. of I. Method A: Refluxing 4.1 g. p-EtOC₆H₄NH₂ and 3.9 g. AcCH₃CO₂Et in 50 ml. C₆H₆ with 1 drop 5% HCl in the app. for the sepn. of H₂O, distg. off the C₆H₆, and distg. the crude product gave in quant. yield p-EtOC₆H₄NHCO₂CH₃ (II), b.p. 140°. Similarly were prepd. p-HOC₆H₄NHCO₂CH₃ (III), m. 89-90° (from EtOH), and o-HOC₆H₄NHCO₂CH₃ (IV), m. 105° starting with p- and o-HOC₆H₄NH₂, resp. Adding 8 g. II to 100 g. of mineral oil stirred and heated to 250°, heating the mixt. 20 min., and allowing the product to crystallize gave a quant. yield of 2-methyl-4-hydroxy-6-ethoxyquinoline, m. 215° (from EtOH). Method B: Treating 2.7 g. o-H₂NC₆H₄Ac in 30 ml. C₆H₆ with 1.6 g. dry C₆H₅N and then dropwise with 3.4 g. p-MeOC₆H₄COCl in 10 ml. C₆H₆N yielded 5 g. o-ArC₆H₄NHCO₂CH₃ (III), m. 129°. Refluxing 2.2 g. III, 30 ml. EtOH, and 36 ml. H₂O,

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treating the soln. with 0.6 g. NaOH in 4 ml. H₂O, refluxing the mixt. 5 hrs., distg. the EtOH, steam distg. the *o*-AcC₆H₄NH₂ formed by hydrolysis, evapp. the residue, acidifying the soln. with HCl, and crystg. the ppt. gave 0.72 g. 2-(*p*-methoxyphenyl)-4-hydroxyquinoline, m. 315°. Method C: Treating a mixt. of 40 g. 3,5-(HO)₂C₆H₃NH₂ (IV), 100 ml. H₂O, and 150 ml. dioxane with 0.4 mole ketene during 1 hr. at room temp., cooling the mixt., and filtering the product gave 47.5 g. 3,5-(HO)₂C₆H₃NHAc (V), m. 213° (from H₂O) (decompn.). Methylation of V with CH₃N, or with Me₂SO, gave 73% or 87%, resp., of 3,5-(MeO)₂C₆H₃NHAc, m. 157° (from H₂O), the hydrolysis of which by refluxing 4 hrs. with 15% aq. alc. NaOH yielded 58% 3,5-(MeO)₂C₆H₃NH₂, m. 46°, bp. 115°. Treating 12.5 g. V in 50 ml. C₆H₅N and 30 ml. H₂O with 17 g. *p*-MeOC₆H₄COCl gave 18.1 g. 3,5-(HO)₂C₆H₃NHCOC₆H₄OMe-*p*, m. 214-15° (decompn.) (from H₂O). Methylation of this product with Me₂SO, in aq. acetone yielded 74% 3,5-(MeO)₂C₆H₃NHCOC₆H₄OMe-*p* (VI), m. 119-20° (from aq. MeOH). Treating 20 g. VI in 200 ml. C₆H₆ with 14.5 g. PCl₅ under cooling, distg. *in vacuo* the C₆H₆ and POCl₃ up to 45°, and dissolving the crude product in 50 ml. PhMe gave a soln. of 3,5-(MeO)₂C₆H₃N:CClC₆H₄Me-*p* (VII). Adding 22 g. VII in 20 ml. PhMe to a mixt. prepd. from 1.8 g. Na dust and 12 ml. CH₃(CO₂Et), in 100 ml. PhMe, refluxing the mixt. 4 hrs., distg. off the volatile products, dilg. the residue with H₂O, and extg. the mixt. with Et₂O gave 3,5-(MeO)₂C₆H₃N:C(C₆H₄OMe-*p*)CH(CO₂Et)₂ (VIII). Heating VIII 5 hrs. at 150-70° gave 40%

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(based on VI) 2-(p-methoxyphenyl)-3-carboxy-4-hydroxy-5,7-dimethoxyquinoline, m. 221° (from EtOH), which yielded by sapon. with 20% alc. KOH 2-(p-methoxyphenyl)-3-carboxy-4-hydroxy-5,7-dimethoxyquinoline, m. 207° (from AcOH). Decarboxylation by heating 30 min. at 220° in vacuo yielded 50% 2-(p-methoxyphenyl)-4-hydroxy-5,7-dimethoxyquinoline, m. 281° (from EtOH), hydrolyzed by refluxing 3 hrs. with 48% HBr to 2-phenyl-4,4',5,7-tetrahydroxyquinoline, m. 348° (from MeOH) (yield 90%). Similar procedure was followed with 2,4-(MeO)₂C₆H₃N: C(C₆H₄OMe-p)CH(CO₂Et), m. 127-8°; 2,4-(MeO)₂C₆H₃N: C(C₆H₄OMe-p)CH(CO₂Et), m. 118° (from EtOH). By the described methods, the following derivs. of I were prepd. (R¹, R², Y, method of prepn., m.p. given): Me, H, H, A, 228°; Me, H, 8-OEt, A, 192°; Me, H, 8-OH, A, 272°; Me, H, 6-OH, A, 270°; Me, H, 6,8-(OMe)₂, A, 221°; Me, H, 6,8-(OH)₂, A, above 300° (decompn.); Ph, H, H, B, 254°; Ph, CO₂Et, 6-OEt, C, 257°; Ph, CO₂H, 6-OEt, C, 269°; Ph, H, 6-OEt, C, 282°; p-MeOC₆H₄, CO₂Et, 6-OEt, C, 232°; p-MeOC₆H₄, CO₂H, 6-OEt, C, above 300° (decompn.); p-MeOC₆H₄, CO₂Et, 8-OEt, C, 173°; p-MeOC₆H₄, CO₂H, 8-OEt, C, 227°; p-MeOC₆H₄, H, 8-OEt, C, 202°; p-MeOC₆H₄, CO₂Et, C, 229°; p-MeO₂IL, CO₂H, H, C, 270°; p-MeOC₆H₄, CO₂Et, 6,8-(OMe)₂, C, 208°; p-MeOC₆H₄, CO₂H, 6,8-(OMe)₂, C, 215°; p-MeOC₆H₄, H, 6,8-(OMe)₂, C, 209°; p-HO-C₆H₄, H, 6,8-(OH)₂, C, 235°.

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Proteins. XXXIII. Differences in the arginine peptides of some serum albumins. Věra Knesslová, Vladimír Kostka, Bořivoj Keil, and František Šorm (Czech. Akad. Věd, Prague). *Chem. Listy* 49, 918-20 (1968); cf. C.A. 49, 10009a. —Human, beef, horse, duck, and sheep serum albumins were subjected to partial hydrolysis by heating 200-mg. portions of the proteins 144 hrs. at 37° with 10 ml. concd. HCl. From the partial hydrolyzates the arginine peptides were isolated by means of the ion exchanger Amberlite IR-A. Hydrolysis of the arginine peptides with equal vols. of concd. HCl (16 hrs. at 105° in a sealed tube), paper chromatography in BuOH-AcOH system, hydrolysis of individual fractions with 6N HCl (16 hrs. at 105°), paper chromatography in the BuOH-AcOH system, and dinitrophenyl analysis revealed considerable differences in the content of the individual amino acids in serum albumins of various origins, although the total hydrolyzates of all of the investigated serum albumins showed only slight differences.

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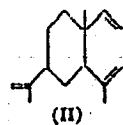
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Terpenes. LXVI. The structure of β -elemene. V.

Sykora, V. Herout, and F. Sorm (Czech. Akad. Vyd. Prague). *Chem. Listy* 40, 942-3 (1955); cf. *C.A.* 49, 14098.

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A hydrocarbon $C_{15}H_{24}$ isolated from sweet-flag and juniper oils and also obtained by pyrolysis of elemol benzoate (I), was named β -elemene and structure II proposed for it.



II isolated from the natural oils, b_p 113-14°, d_4^{20} 0.8802, n_D^{20} 1.4913, $[\alpha]_D^{20}$ -10.0°. Its ozonization gave 3.2 moles CH_2O . I, purified by heating the crude product 1 hr. at 90-100° with MeOH, b_p 160°, was decompd. by heating (15.6 g.) at 100 mm. and 210-40° to give 7.4 g. crude and 3 g. pure IV, b_p 128-9°, d_4^{20} 0.8803, n_D^{20} 1.4949, $[\alpha]_D^{20}$ -11.1°.

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Mechanism of antibiotic action. VII. Changes in the level of phosphorylated intermediates in *Escherichia coli* cultivated in the presence of chloramphenicol, oxytetracycline, and chlortetracycline. Feinštok Sorma and Jilina Černá (Zech. Akad. Věd., Prágu: Chem. Listy 49, 1037-63(1955); cf. C.A. 49, 12591d. — The content of adenosine triphosphoric acid (I) and of other phosphorylated intermediates in *E. coli* depends on the compn. of the substrate and does not change essentially during growth. The content of I is considerably decreased in bacteria cultivated in the presence of oxytetracycline and of chlortetracycline in concns. partly inhibiting the propagation. The presence of chloramphenicol under the same conditions has no effect on the content of I. M. Hudlický.

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✓ Mechanism of antibiotic action. VIII. Changes in the free amino-acid metabolism of *Escherichia coli* during the growth in the presence of chloramphenicol. Jan Škoda and František Šorma (Czech. akad. vtd, Prague). *Chem. Listy* 49, 1221-7 (1955); cf. C.A. 49, 13300c. — A strain of *E. coli* which is resistant to chloramphenicol excretes into the medium during growth amino acids the amt. of which is proportional to the concn. of the antibiotic. During bacteriostasis practically all of the assimilated N is contained in the excreted amino acids. The amino acids have L-configuration. The cells of the resistant strain of *E. coli* contain free glutamic acid in addn. to small amts. of alanine and valine. M. Hrdlička

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Virus studies. VII. A comparative study of two strains of the tobacco mosaic virus. Alexander Jakubovič, Libor Šlecht, Bohuš Keil, and František Šorm (Czech. Akad. Věd, Prague). *Chem. Listy* 49, 1581-4 (1955); cf. C.A. 49, 10440s. — Ultraviolet spectrum, electrophoretic mobility, and qual. and quant. content of amino acids are given for cryst. forms of the ordinary strain and Alke-strain of the tobacco mosaic virus. Only the Alke-strain was found to contain histidine. Electron-microscope photographs of both cryst. forms are given. M. Hudlický — (3)

František, Šorm

CZECHOSLOVAKIA/Organic Chemistry. Natural Substances
and Their Synthetic Analogues.

E-3

Abs Jour: Ref Zhur - Khimiya, No. 8, 1957, 26969.

Author : Jóska, Jiří, Šorm, František.
Inst :
Title : Steroids. XX. Some Nitrogen Containing Ana-
logues of Androgenous Hormones.

Orig Pub: Chem. listy, 1955, 49, No. 11, 1687 - 1692;
Sb. chekhosl. khim. rabot, 1956, 21, No. 3,
754 - 760.

Abstract: Δ^4 -3 ξ -17 β -diaminoandrostene (I), Δ^4 -3- ξ amino-17 β -oxyandrostene (II), the same hydrogenated to 3 β -amino-17 β -oxyandrostane (III), 3 β -amino-17 β -oxyandrostane (IV) and Δ^4 -3 ξ -aminoandrostene (V) were obtained by reducing oxides of corresponding keto-derivatives.

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APPROVED FOR RELEASE: 08/25/2000 CIA-RDP86-00513R001652420015-5

do not possess any physiological activity.
(5 hours, 175°) 10 hours with 8 g of formamide
and 12 ml of 80% aq. HCOOH, Δ -17 β -formilamino-
androstene-3 β was prepared, yield 70%, melting
point 260 to 265° (from dioxane), from which
 Δ^4 -17 β -formilaminoandrostene-3, melting point
221 to 222° (from ethylacetate), $[\alpha]_D^{20} + 86^\circ$
+ 3° (c 1.9; chlorof.), was produced (yield 73%)
by oxidation with cyclohexanone in presence of
Al isopropylate in toluene at 150°. By boiling
this product 2 hours with alcohol containing
20% of HCl, chlorohydrate of Δ^4 -17 β -amino-
androstene-3, melting point 333 to 335° (dis-
soc., from water), was received, which produced

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Abs Jour: Ref Zhur - Khimiya, No. 8, 1957, 26969.

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Abs Jour: Ref Zhur - Khimiya, No. 8, 1957, 26969.

derivative (bis-IP), melting point 176 to 177°
(from acetone); dibenzilidene derivative (di-
BD), melting point 198 to 199° (from alc.).
Acetate of II, melting point 186 to 190° (alc.-

eth.), $[\alpha]_D^{20} +38^\circ \pm 3^\circ$ (c 1.0; in alc.), was
analogously obtained from Δ^4 -androstenole-
17 β -one-3 oxime; chlorohydrate, melting point
318 to 320° (dissoc. from alc.); IP, melting
point 182 to 184° (from acetone), B), melting
point 205 to 206° (alc.). Acetate of III was
obtained by hydrogenation of II in CH₃COOH
on Pt. In view of the fact that the deriva-
tives of III are not identical to the derivatives
of IV, the authors ascribe the above mentioned

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Abs Jour: Ref Zhur - Khimiya, No. 8, 1957, 26969.

structure or the structure 3 α - or 3 β -amino-
testanole-17 β to III. The melting point of III

is 173 to 178° (from alc.-eth.) and $[\alpha]_D^{20}$ is +
34° \pm 3° (c 1.0; in alc.); BP, melting point 190
to 191° (from alc.). Boiling of 800 mg of an-
drostanole-17 β -one-3 oxime in 60 ml of alcohol
with 2 g of Na results in 420 mg of IV, melting

point 170 to 171° (from eth.), $[\alpha]_D^{20} +58^\circ \pm$
3° (c 0.90; in chlorof.). The β -configuration
of the amine group in IV was accepted by the
authors analogously with other examples (see
RZhKhim, 1956, 6909). IV acetate, melting point

199 to 204° (from alc.-eth.), $[\alpha]_D^{20} +89^\circ \pm 3^\circ$

Card 5/6

✓ Metabolism of neoplastic tissues. II. Glycolysis of
cell-free extracts of the Ehrlich ascites tumor. Libor
Šlecht, Alexander Jakubovík, and František Šorm (Chem.
listav Čal. akademie věd, Prague). *Chem. Listy* 49, 1706-9
(1955); cf. *C.A.* 49, 10493d.—A cell-free ext. prepd. from
the Ehrlich ascites tumor glycolyzes glucose at the same rate
as intact cells but does not glycolyze glycogen. No glycogen
phosphorylase was found in the ext. The results show that
no glycogen is present in the cells of the above tumor.
M. Hudlický

(2)

Sorm, František

Mechanism of antibiotic action. IX. The effect of chloramphenicol on the enzyme systems oxidizing acetic, pyruvic, and oxalacetic acids in *Escherichia coli*. Dezider Grünberger, Vilém P. Hess, and František Sorm (Czech. Akad. věd, Prague). *Chem. Listy* 49, 1710-16 (1955); cf. C.A. 49, 14890e.—Enzymic systems oxidizing AcOH and $\text{CO}_2\text{HCOCH}_2\text{CO}_2\text{H}$ (I) are present only in cells cultivated during aeration. Bacteria cultivated stationarily form these systems only in the presence of the appropriate acids and O_2 . The synthesis is inhibited by chloramphenicol (II). The stationary cultures of *E. coli* oxidize AcCO_2H to AcOH, and after adaptation, to CO_2 and H_2O . The bacteria cultivated in low concns. of II stop the oxidation at the AcOH stage. II has no effect upon bacteria cultivated during aeration. Bacteria resistant to II and cultivated stationarily oxidize AcCO_2H 50% as rapidly as the cells cultivated with aeration and 20% more rapidly than the sensitive strains. AcOH is oxidized slower by resistant strains than by sensitive ones in all cases.

M. Hudlický

(2)

Czechoslovakia/ Organic Chemistry - Naturally occurring substances
and their synthetic analogs

E-3

Abs Jour : Referat Zhur - Khimiya, No 4, 1957, 11823

Author : Kovacs Odon, Herout Vlastimil, Horak Milan, Sorm Frantisek
Title : On Terpenes. LXVII. Hydrogenation Products of Santonin and Alantolactone

Orig Pub : O terpenech. LXVII. Hydrogenacni produkty santoninu a alantolaktonu.
Chem listy, 1955, 49, No 12, 1856-1869 (Czech); Sb. chekhosl. khim.
rabot, 1956, 21, No 1, 225-239 (English)

Abstract : On hydrogenation of santonin (I) under different conditions, are formed three isomers of 3-ketosantonolide-5,12 (IIa, b and c), and on further hydrogenation there are obtained the corresponding 3-hydroxysantonolides-5,12 (IIIa, b, c). On reduction according to Clemensen, IIa and IIc give santonolide-5,12 (IVa), while IIb is converted to santonolide-5,12 [sic/ (IVb). On interaction of IIa, b and c with ethylenedithiol (V) there are obtained ethylene thioketals, which on desulfurization with skeleton N1 form, respectively, IVa, b and c. IIc is readily isomerized to IIa. LiAlH_4 reduces IVa to santandiol-5,12 (VI), and alantanolide-5,12 (VII) to alantandiol-5,12 (VIII). Presented are the

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Abs Jour : Referat Zhur - Khimiya, No 4, 1957, 11823

infrared spectra of IVa, b and c, VII, IIa, b and c, IIIc, VI, VIII, 5,12-oxidosantan (IX) and alanten- Δ (?) -ol-12 (X). On hydrogenation of 0.1 mole I in 200 ml CH_3OH with Pd/BaCO_3 IIa is obtained, yield 74%, MP 158° , $[\alpha]_D^{18} + 30^\circ \pm 1^\circ$ (c 5.0) (all $[\alpha]_D$ determined in chloroform); mother liquors of IIa are evaporated, residue dissolved in aqueous NaOH, after acidification ether is used to extract 3-keto-5-hydroxy-santanic acid (XI), yield 10.8%, MP $190-192^\circ$ (from 50% CH_3OH), $[\alpha]_D^{20} + 20.7^\circ \pm 1^\circ$ (c 7.45). Solution of 2 g XI and 0.5 g p-toluene sulfonic acid (XII) in 50 ml CH_3COOH held for 5 hours, diluted with water and extracted with ether to recover IIb, yield 89%, MP $103-105^\circ$ (from 70% CH_3OH), $[\alpha]_D^{21} + 11.3^\circ \pm 1^\circ$ (c 3.88). By hydrogenation of IIb in glacial CH_3COOH with PtO_2 is obtained IIIb. MP $213-215^\circ$ (from CH_3OH), $[\alpha]_D^{20} - 8.5^\circ \pm 1^\circ$ (c 4). 4 g I are hydrogenated in CH_3OH with PtO_2 (120 atm, 20°), to get IIIc, yield 44%, MP 135° (from 50% CH_3OH), $[\alpha]_D^{20} + 42.7^\circ \pm 1^\circ$ (c 3.97). Mixture 0.66 mole CrO_3 , 0.1 ml water, 1 mole IIIc and 6 ml CH_3COOH left standing 20 hours, diluted with water (6 ml) and several drops alcohol, evaporated, and ether extraction

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gives IIc, MP 145-146°, $[\alpha]_{20D} + 77.5 \pm 2^\circ$ (c 5.12). 0.01 mole IIa reduced according to Clemmensen (8 g Zn; 21 ml HCl; 1:2, boiled 12 hours), ether extraction gives IVa, yield 93%, MP 154° (from 90% alcohol), $[\alpha]_{20D} + 26.8 \pm 1^\circ$ (c 4.45). In the same manner from IIb is obtained IVb, yield 70%, MP 86-87° (from alcohol), $[\alpha]_{20D} - 27.9^\circ \pm 2^\circ$ (c 3.8). 100 mg IIc boiled 12 hours with 4 ml HCl (1:2), to get 65 mg IIa. Mixture of 0.01 mole IIa, 50 ml glacial CH_3COOH , 0.01 mole V and 0.96 g XII, held 3 hours at 20°, poured on ice, to get ethylene thioketal IIa, yield 99%, MP 195-196° (from ethyl acetate), $[\alpha]_{20D} + 44.7^\circ \pm 1^\circ$ (c 4.95), which (0.005 mole) on boiling for 8 hours in 120 ml dioxane with 15 ml skeleton Ni I gives IVa with yield 98%. Analogously from IIb is prepared ethylene thioketal, yield 81%, MP 122-123° (from CH_3OH), $[\alpha]_{20D} - 11.08^\circ \pm 1^\circ$ (c 6.32), and from it IVb, yield 95%. Under the same conditions IIc is converted over the ethylene thioketal (yield 95%, MP 166-167° (from ethyl acetate), $[\alpha]_{20D} + 37.9^\circ \pm 1^\circ$ (c 3.95)) into IVc, MP 137-139° (following crystallization from alcohol and di-iso-propyl ether, and sublimation (12 mm,

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Abs Jour : Referat Zhur - Khimiya, No 4, 1957, 11823

110°), $[\alpha]_D^{20} + 92.2 \pm 2^\circ$ (c 3.73). Mixture of 0.1 mole LiAlH_4 , 0.05 mole IVa and 600 ml ether is stirred 2 hours, decomposed with 6 ml water and 200 ml 25% H_2SO_4 , and VI is extracted with ether, yield 98%, MP 154-155° (from benzene), $[\alpha]_D^{20} 25.3^\circ \pm 1^\circ$ (c 4.12 in chloroform- CH_3OH , 1:1). 2 mole VI dissolved at 0° in 5 ml SOCl_2 , after 1.5 hour SOCl_2 driven off, following chromatography on Al_2O_3 (petroleum ether) there are obtained 180 mg cyclic sulfite of VI, MP 75-76° (from alcohol), $[\alpha]_D^{20} -253^\circ \pm 2^\circ$ (c 2.84), which is saponified in aqueous-alcoholic NaOH to get VI. Boiling for 30 minutes of 2.5 mmole VI with 0.1 g XII in 12 ml C_6H_6 gives IX, yield 84%, BP 132-133°/8 mm, $n_D^{20} 1.4972$, $d_4^{20} 0.9788$, $[\alpha]_D^{20} -39.54^\circ$. On steam distilling 3 kg of Inula Helenium roots, crystallizing the distillate from 70% alcohol and hydrogenating the product at 45° with PtO_2 , in ethyl acetate, there are obtained 16.3 g of VII, MP 147-147.5° (from alcohol), $[\alpha]_D^{18} + 14.6 \pm 1^\circ$ (c 1.92). On reduction of VII with LiAlH_4 VIII is obtained, yield 93%, MP 111-112° (from benzene-petroleum ether, 1:3), $[\alpha]_D^{20} -6.2 \pm 1^\circ$ (c 4.55). VIII is converted to cyclic sulfite (like VI) yield 47%, MP

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Abs Jour : Referat Zhur - Khimiya, No 4, 1957, 11823

114-116° (from alcohol) $[\alpha]^{20}_D - 52.4^\circ \pm 2^\circ$ (c 3.62). By dehydration under conditions used for IX, there is obtained from VIII the X, yield 88%, BP 133-135°/8 mm, $n^{20}_D 1.5078$, $d^{20}_4 0.9879$, $[\alpha]^{20}_D - 32.7^\circ \pm 2^\circ$.

Card 5/5

FRANTISEK, SORM

Czechoslovakia/ Organic Chemistry - Naturally occurring substances
and their synthetic analogs

E-3

Abs Jour : Referat Zhur - Khimiya, No 4, 1957, 11824

Author : Sychy Milos, Herout Vlastimil, Sorm Frantisek

Title : On Terpenes. LXVIII. Formation of Two Tetraalkyl Azulenes on Treatment
of Wormwood.

Orig Pub : O terpenech. LXVIII. Vznik dvou tetraalkylazulenu pri zpracovani pelyn-
ku praveho. Chem. listy, 1955, 49, No 12, 1870-1878 (Czech); Sb. chek-
hosl. khim. rabot, 1956, 21, No 2, 477-486 (English; Russian summaries)

Abstract : Technical mixture of azulenes, that is obtained on treatment of worm-
wood with alkali, was separated, by countercurrent extraction with pe-
troleum ether and 52 2% solution of H_3PO_4 , yielding two new azulenes:
 $C_{16}H_{20}$ (I), recovered from the petroleum ether, and $C_{15}H_{18}$ (II), isola-
ted from the phosphoric acid fractions. On oxidation of I and II with
 $KMnO_4$, were obtained acetic and propionic acids. It is shown that by
heating (24 hours) of wormwood extracts with 10% solution of NaOH the-
re is obtained hamazulene, while heating them in the presence of worm-
wood stems yields I and II. II and I are formed on alkaline alkylation

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Czechoslovakia/ Organic Chemistry - Naturally occurring substances
and their synthetic analogs

Abs Jour : Referat Zhur - Khimiya, No 4, 1957, 11824

of hydroxy-guaiadienolide (III) and absinthin (IV), respectively, with HCHO and CH_3CHO . On hydrogenation of I and II in CH_3COOH with PtO_2 , decahydro-derivatives are formed. On this basis the authors attribute to I the structure 1,4-dimethyl-2,7 or 6,7-diethylazulene, and to II that of 1,2,4- or 1,4,6-trimethyl-7-ethylazulene. For comparison were synthesized 1,4-dimethyl-7-sec-butylazulene (V) and 1,4-dimethyl-3,7-diethylazulene (VI). From 0.7 g technical mixture of I and II were isolated 0.254 g I, BP $173^\circ/9$ mm; trinitrobenzolate (TNB), MP 133° (from alcohol), and 0.16 g II, BP $160^\circ/11$ mm; TNB, MP 150° (from alcohol). Mixture of 50 mg III with 20 mg 30% HCHO and 100 ml 10% NaOH is heated 20 hours at 100° , after acidification the azulene is removed by steam distillation, and from it II is isolated with petroleum ether over Al_2O_3 . Mixture of sec- $\text{C}_4\text{H}_9\text{Li}$ (from 2/ g sec- $\text{C}_4\text{H}_9\text{Cl}$, 2.2 g Li and 50 ml petroleum ether) and a solution of 2.2 g 2,8-dimethyl-(0,3,5)-bicyclo-decanone-5 in 30 ml ether, is boiled 6 hours, decomposed with water and dilute H_2SO_4 , and from the ether extract is isolated 2,8-dimethyl-5-sec-butyl-(0,3,5)-bicyclodecanol-5 (VII), yield 39%, BP $157^\circ/9$ mm.

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Czechoslovakia/ Organic Chemistry - Naturally occurring substances
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APPROVED FOR RELEASE: 08/25/2000

CIA-RDP86-00513R001652420015-5"

Abs Jour : Referat Zhur - Khimiya, No 4, 1957, 11824

On heating 1 g VII with 1.5 g KHSO_4 (180° , 20 minutes) is obtained 2,8-dimethyl-5-sec-butyl-(0,3,5)-bicyclodecene (VIII), d_4^{20} 0.8813. Mixture of 0.6 g VIII and 0.35 g S is heated 15 minutes at 180° , the product is subjected to chromatography on Al_2O_3 , and petroleum ether is used to eluate V, yield 11%; TNB, MP 126° (from alcohol). Mixture of 0.4 g hamazulene, 50 ml CH_2Cl_2 , 8.2 ml $(\text{CH}_3\text{CO})_2\text{O}$ and 1.5 ml BF_3 etherate, allowed to stand for 48 hours; CH_2Cl_2 extract washed with water and after removal of solvent subjected to chromatography on Al_2O_3 ; benzene is used to eluate 0.25 g 3-acetyl-hamazulene (IX); TNB, MP 123° (from alcohol). Mixture of 0.22 g IX, 30 ml ether and 0.15 g LiAlH_4 , after standing for 24 hours, is decomposed with 100 ml water, and the ether extract, after removal of the ether, is subjected to chromatography on Al_2O_3 ; petroleum ether is used to eluate VI; TNB, MP 148° (from alcohol). Presented are ultraviolet spectra of I, II, V and VI, infrared spectra of I, II and their decahydro-derivatives, and of V, as well as the visible spectra of I, II and V.

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FRANTISEK, SORM

Czechoslovakia/ Organic Chemistry - Naturally occurring substances
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Abs Jour : Referat Zhur - Khimiya, No 4, 1957, 11825

Author : Romanuk Miroslav, Herout Vlastimil, Sorm Frantisek
Title : On Terpenes. LXIX. Structure of Dehydrokostuslactone.

Orig Pub : O terpenech. LXIX. Konstituce dehydrokostuslaktону. Chem. listy, 1955,
49, No 12, 1879-1885 (Czech); Sb chekhosl. khim. rabot, 1956, 21, No 4,
894-901 (English; Russian summaries)

Abstract : Dehydrokostuslactone (I) (from Saussurea lappa Clarke) yields on hydro-
genation a hexahydro-derivative (II), which was identified, by its in-
frared spectrum, as guaianolide (see RZhKhim, 1954, 27127). On dehydro-
genation of I gives hamazulene (III), while dehydrogenation of II
yields a mixture of S-guaiazulene (IV), Se-guaiazulene (V), III and
2,4-dimethyl-7-ethylazulene (VI). Ether solution of kostus oil was was-
hed with bicarbonate, saponified by boiling with NaOH, solution of the
salts washed with ether, and by acidification reconverted into lactone,
which was washed free from phenols with cold alkali; thus was obtained
I, BP 140-143°/0.5 mm, MP 61°, $[\alpha]_D^{20}$ - 12.9°. On hydrogenation of I

Card 1/2

SHORM, F.

USSR/ Agriculture - Antibiotics

Card 1/1 Pub. 22 - 33/54

Authors : Shorm, F. Academician of Czech Acad. of Sc.; and Zelinkova, M.

Title : The mechanism of the action of antibiotics on the development of plant shoots

Periodical : Dok. AN SSSR 100/3, 525-528, Jan 21, 1955

Abstract : Experiments were conducted to determine the morphological effect of D-chloramphenicol (antibiotic substance) on the growth of plant shoots. It was established that this antibiotic produces a nonspecific effect on certain general processes of plant metabolism as well as on the metabolism of living organisms. Twelve references: 3 Czech, 2 USA, 2 Swiss, 2 French, 1 Italian and 2 Swedish (1943-1954). Tables.

Institution : Academy of Sciences Czechoslovakia, Institute of Organic Chemistry, Biochemical Section, Prague

Presented by : Academician A. I. Oparin, November 13, 1954

SHORN, F.

Synthesis of proteases and amylase in mouse pancreas in vitro. I. Rykhlik, Yu. Shveltsar, and F. Shorn. *Doklady Akad. Nauk S.S.S.R.* 104, 233-6 (1956). The pancreas of white mice *in vitro* is capable of synthesizing proteases and amylase during incubation in Krebs bicarbonate medium with 0.2% glucose in contact with O_2 and 5% CO_2 at 40° . The synthesis is relatively slow during the 1st hour, but accelerates over the following 2 hrs. Total acid hydrolyzate of casein enriched with tryptophan, or partial enzymic hydrolyzate of casein can serve as the source of the needed amino acids. The optimum concn. of these sources is 0.2-0.3%. Anaerobic conditions and dinitrophenol block the enzyme synthesis. In absence of external source of NH_4 , the endogenous synthesis takes place, amounting to 10-30% of the possible total. This is similarly blocked by anaerobic conditions and dinitrophenol. *O*-Diazocetylserine is a powerful blocking agent as well; *DL*-ethionine has no effect, but *D*-chloramphenicol was but feebly effective.

G. M. Kosolapoff

MD

(2)

CZECHOSLOVAKIA/General Problems of Pathology. Neoplasms.

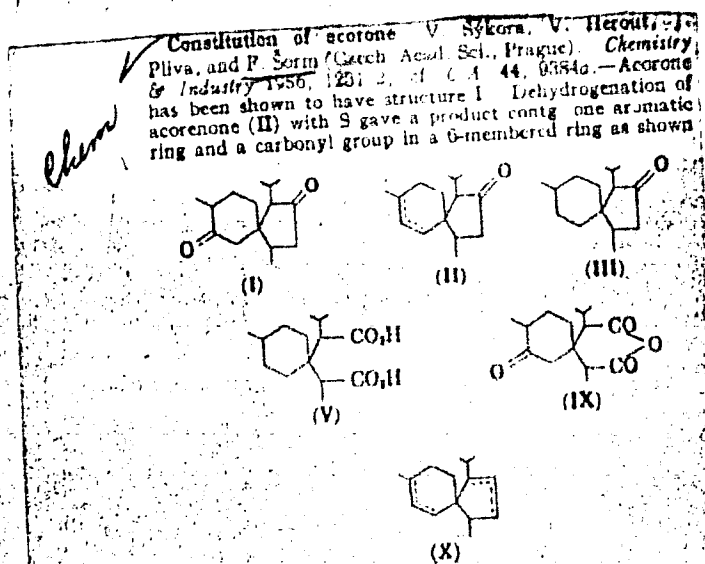
Abs Jour: Ref Zhur-Biol., No 8, 1958, 37242.

Author : Zhlekhta, L., Yakubovich, A., Shorn, F.
Inst :
Title : The Cancerostatic Action of 6-Azaauracil.

Orig Pub: Chemotherapeutika, 1. Farmac. sympos, Praha, 1956, 29.

Abstract: For a period of 6 days 5 mg doses of 6-azauracil were injected in mice, beginning within 24 hours after intra-peritoneal grafting with the ascitic cancer of Ehrlich. Comparative simultaneous studies, under identical conditions, were made with 6-mercaptopurine. Judging from the survival rate of the animals, both preparations inhibited the growth of the tumor to the same degree.
(20%)

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by an absorption band at 1714 cm^{-1} . This indicated that the C atom common to the 5- and 6-membered rings is

SYKORA, V., HEROUT, J. P., ŠORM, F.

quaternary, since aromatization did not take place without rearrangement. Acoranone (III) was converted to a hydroxymethylene deriv. (V) which on oxidation yielded V. Catalytic dehydrogenation of V gave a mixt. of p -MeC₆H₄Et (VI) and p -MeC₆H₄CH₂CHMe₂ (VII) together with EtCO₂H and Me₂CHCH₂CO₂H. I and H₂I gave a benzylidene deriv. (VIII) which on ozonolysis gave IX, m. 127.5°. Pyrolysis of the Ba salt of IX gave a mixt. of 2 α , β -unsatd. ketones which were converted in 4 steps to VI and VII. Dehydrogenation of isoacordiene (X) produced 1,7-dimethyl-4-isopropyl-naphthalene. Acorone is the first naturally-occurring compd. shown to have a spirane skeleton.

J. H. Losperst

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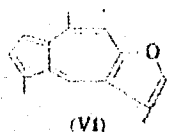
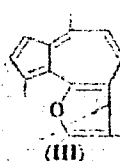
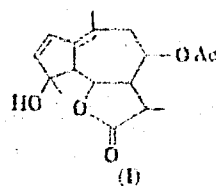
2/2

SORM, F.

Structure of matricin? 2. Čekan, V. Herout, and B. Sorm (Czech. Acad. Sci., Prague). *Chemistry of Industry* 1950, 1234-57. *Chem. Abstr.* 44, 8011, 5604f. The probable constitution of the chamazulene precursor previously isolated from *Matricaria chamomilla* is given as 1-hydroxy-6-acetoxyguai-2,4(10)-diene-8,12-diolide (I). The name matricin is suggested for I. Hydrogenation of I over Pt in HOAc gave two 6-acetoxyguaianolides, m. 115.5° and 123°, resp. Treatment of the lower-melting isomer with K₂CO₃ in MeOH gave 6-hydroxyguaianolide, m. 157°, which was oxidized with CrO₃ in HOAc to the oxoguaienolide, m. 111-12°. The latter was converted via the ethyl methylethylketol, m. 145-6°, and desulfurization with Raney Ni to 8,12-guaienolide (II), b.p. 130-5° (bath temp.). Reduction of II with LiAlH₄ gave 8,12-guaienediol, which on dehydrogenation with Se at 280-300° gave artemizulene (III). Hydrogenation of I in EtOH gave 1-hydroxy-6-acetoxy-8,12-guaienolide (IV), m. 100.6-9.0°. Hydrolysis of IV formed the 1,6-dihydroxyguaianolide (V), m. 138.6-40°. Reduction of IV with LiAlH₄ in boiling Et₂O gave the lactol, m. 148-52°, which on dehydrogenation gave III. Reduction of IV with LiAlH₄ in boiling N-ethylpiperidine gave 1,6,8,12-guaienetetrol, m. 138-9°, which on dehydrogenation gave a mixt. of III and linderazulene (VI). IV was stable towards CrO₃ in HOAc, but V under the same conditions gave 1-hydroxy-6-oxoguaienolide, m. 187.5-9.0°, which was dehydrated with HCO₂H to the oxoguaienolide, m. 190-1°. The double bond formed in this reaction was not conjugated with the

Čekan, Z., Herout, V., Šturm, F.

lactone or ketone carbonyl as shown by ultraviolet and infrared spectra.



R. H. Lippert

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RMK.

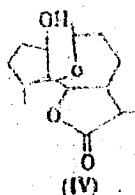
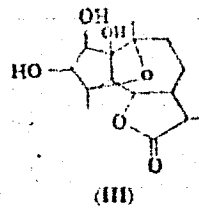
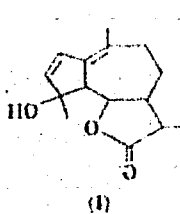
Scim, F.

7
The structure of artabsin, the prochamazulenogen from *Artemisia absinthium*, V. Herout, L. Dolejš, and F. Sorm (Czech. Acad. Sci., Prague). *Chemistry & Industry* 1958, 1238; cf. C. Z. 45, 8604a. Artabsin, the chamazulene precursor previously isolated from *Artemisia absinthium*, is shown to have the constitution 1-hydroxyguai-2,4(10)-dien-8,12-olide (I). Hydrogenation of I on Pt in EtOH gave a dihydro deriv. (II) with the 4(10) double bond retained. Hydrogenation with Pt in HOAc gave a mixt. which was resolved by chromatography into 8,12-guainolide, m. 90°, and 3 stereoisomeric 1-hydroxyguainolides, m. 103-9°, 150-60°, and 130°, and $[\alpha]_D^{25}$ 0°, -8.9°, and 30.4°, resp. The latter compds. were inert to CrO₃ and hence contained tertiary OH groups. Dehydrogenation of the product, m. 103-9°, with SOCl₂ in pyridine gave an impure product which was shown by ozonolysis to contain 30% of an isomer with a terminal methylene group. I was oxidized by KMnO₄ to III, m. 158°. Periodate oxidation of III pointed to the presence of the vicinal triol. Hydrogenolysis of the ozonide of II provided IV, m. 160°, which on oxidation with CrO₃ in HOAc gave the corresponding ketone, m. 145°. The latter showed absorption at 1735 cm.⁻¹, indicative of a carbonyl group in a 5-membered ring. I is closely related structurally to arboresecin (cf. Muzur and Meisels, C.A.

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Herout, V., Deleij, L., Sorm, F.
51, 4320f) and to matrixin (cf. following abst:).



R. H. Looper

2/2

PMK

SORM, F., akademik; SKODA, J.

Antibacterial action of ethyl ether of diazopyruvic acid and its
antagonism to leucine (isoleucine) in Escherichia coli. Dokl. AN
SSSR no.2:291-294 Mr '56. (MIRA 9:7)

1.Chekheslevatskaya Akademiya nauk (for Sorm).2.Biohimicheskoye
otdeleniye Khimicheskogo instituta Chekheslevatskoy Akademii nauk,
Praga. Predstavleno akademikem A.I.Oparinym.
(PYRUVIC ACID) (ESCHERICHIA) (LEUCINE)

SHORMOVA, Z.; SHORM, P.; BAUYEROVA, Ya.; ZELINKOVA, M.

Stimulating action of 5-bromouracil on higher plants [with English summary in insert] Fiziol.rast. 3 no.3:204-207 My-Je '56.

(MLRA 9:9)

1. Biokhimicheskiye otdeleniye Khimicheskogo instituta Chekhesleva-
tskey Akademii nauk, Praga.

(Uracil) (Growth promoting substances)

SCRM, F.

✓ The anticancerous action of 6-azauracil. F. Sorm, A. Jakubovic, and L. Slechta (Czech. Acad. Sci., Prague). *Experientia* 12, 271-2(1956)(in English).—Treatment of mice with 250 mg./kg. 6-azauracil (3,6-dioxo-2,3,4,6-tetrahydro-1,2,4-triazine)/kg. body wt. daily caused a prolongation of life following injection 4×10^5 Ehrlich ascites carcinoma cells. This prolongation of life was similar to that obtained by treatment with 30 mg. 6-mercaptopurine/kg. body wt. daily. — J. S. Farner

3

SORM, FRANTISEK

Metabolism of neoplastic tissues. II. Glycolysis of
cell-free extracts of the Ehrlich ascites tumor. Libor
Slecht, Alexander Jakubovič, and František Šorm. Col-
lection Czechoslov. Chem. Commun. 21, 24-7(1956)(in
German).—See C.A. 50, 2025e. R. J. C.

3

SORM, FRANTISEK

✓ Virus studies. VII. A comparative study of two strains
of the tobacco mosaic virus. Alexander Jakubovič, Libor
Slechtal, Botivoj Keil, and František Sorm. Collection
Czechoslov. Chem. Commun. 21, 20-32 (1958) (in German).
See C.A. 50, 440a.
R. J. C.

4

SORM, F.

SORM, F. Mechanism of the action of antibiotics. VII. Measurement of the content of phosphorylated intermediate products of Escherichia Coli during cultivation in the presence of chloramphenicol, oxytetracycline, and chlortetracycline. In Russian. p. 55. Vol. 21, no. 1, Feb. 1956. SBORNIK CHEKOSLOVATSKIKH KHMICHESKIKH RABOT. COLLECTION OF CZECHOSLOVAK CHEMICAL COMMUNICATIONS. Praha, CZECHOSLOVAKIA.

SOURCE: EAST EUROPEAN ACCESSIONSLIST (EEAL) VOL 6 NO 4 April 1957

SORM, FRANTISEK.

Chem Terpenes. LXVII. Hydrogenation products of nantonin
and alantolactone. Odon Kováč, Vlastimil Horáček,
Milan Horák, and František Sorm. *Collection Czechoslov.*
Chem. Commun. 21, 250-253 (1966) (in English). See C.A.
50, 93425d. E. J. C.

4

Arginine metabolism in birds. J. Bauerova and P. Sorm (Chem. Inst., Czechoslov. Acad. Sci., Prague). *Biokhimiya* 21, 397-402(1956).—Studies were made on pigeons, chickens, *Perdix perdix*, *Phasianus colchicus*, *Corvus frugilegus*, *Garrulus glandarius*, *Pica pica*, *Colinus monedula*, *Larus ridibundus*, and *Verreauxia tinamulus*. 2

In the liver in *C. frugilegus*, *G. glandarius*, *C. tinamulus*, arginase of high activity is present, but the activity of glycine transaminase is low. In chickens arginase activity is low and glycine transaminase is high. In similar studies with birds in a state of starvation, it was shown that the activity of arginase was found to be higher than normal in all birds, and in the liver of chickens, in which under normal conditions of nutrition no arginase is present, it was found at a high level under starvation. In the starving *P. perdix* arginase was even higher. B. S. Levine

SORM, F.

~~SORM, F.~~

✓ Arginine metabolism in birds. Ya. Bauerova and F.
Sorm. *Biochemistry (U.S.S.R.)* 21, 401-5 (1956) (English
translation). See *C.A.B.* 59, 172161. D. M. K.

2

SORM F. 10

SORM, F.

✓ Terpenes. LXVIII. Formation of two tetraalkylarulenes
in the working up of wormwood. M. Suchý, V. Herout,
and F. Šorm. Collection Czech. Chem. Commun. 21, 477-
86(1956)(in English).—See C.A. 50, 9343g. LXIX. The
constitution of dehydrocostuslactone. M. Románek, V.
Herout, and F. Šorm. Ibid. 894-901(in English).—See
C.A. 50, 9344d. E. J. C.

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30 RM, F. 1111
7/24 6-Azauracil, an antimetabolite of uracil and cytosine in
Escherichia coli. Preliminary communication. P. Šorm
and J. Skoda. Collection Czech. Chem. Commun. 21, 487-8
(1956)(in English).—See C.A. 50, 10349h. E. J. C. 2

Sorm, F.

Stimulating effect of peptides on enzyme synthesis in the mouse pancreas *in vitro*. I. Rychlík and F. Sorm (Czech. Acad. Sci., Prague). *Biochim. et Biophys. Acta* 21, 600-1 (1959) (in English).—Peptic hydrolyzates of chymotrypsinogen contain a factor which stimulates protease synthesis in the pancreas *in vitro*. This, or another stimulating factor, is also present in pancreatic tissue, and its amt. therein is decreased by preincubation. The factor is probably peptidic, corresponding to one or more peptides of the peptic digest. Peptic hydrolyzates of other proteins also stimulate pancreatic enzyme synthesis *in vitro*, to varying extents.

W. L. S.

Morton Pader

2

SC 11A, F.

Proteins. XXXV. Specificity of pancreatic proteinases in
the hydrolysis of clupeine V. Tomásek, B. Keil, and P.
Sorm. Collection Czech. Chem. Commun. 21, 1035-42
Prague (German) —See C.A. 50, 0481g. E. I. S.

3

SOR M, F.

WIA ✓ Changes in the ribonucleic and deoxyribonucleic acid content in the organs of the pea during germination. Z. Sor-mová and P. Sorin. Collection Czech. Chem. Commun. 21, 1043-8 (1956) (in German).—See C.A. 50, 9532a. E. J. C.

2

SORM, F

Changes in the adenosinetriphosphate content during
termination of the lens. K. Sebesta and P. Sorm. *Col-
lection Czech. Chem. Commun.* 21, 1047-53 (1956) (in Ger-
man). See C.A. 50, 9532c. E. J. C.

Serm F

Reference LXXI HelenaBa lactone of the guano-
side group. V. Hermit, M. Roushuk, and E. Serm
Section Czech Chem Commun: 21, 1359-62 (1972) No. 1
(ish) Sec C A 50, 167105

Bm
MT

SORM, FRANTISEK

Metabolism of neoplastic tissues. III. Effect of 2-deoxyglucose on anaerobic glycolysis in the Ehrlich ascites tumor. Libor Slechta, Alexander Jakubovič, and František Sorm (Čsl. akad. věd, Prague). *Chem. Listy* 50, 125-32(1956); cf. *C.A.* 50, 2025e.—2-Deoxyglucose (I) inhibits glucolysis and fructolysis in the cells of the Ehrlich ascites tumor and in the cell-free ext. prepd. therefrom. Instantaneous fructolysis occurs when the concn. ratio of fructose (II) to I is 1:0.1, glucolysis when the ratio of glucose (III) to I is 1:8. I inhibits competitively hexokinase located in the cell wall which phosphorylates III during its passage through the cell wall. II penetrates into the cell by diffusion only, contrary to glucose. Intracellular hexokinase phosphorylates I. M. Hudlický

HD

(2)

SNOD, P. - Isolation of pure ascortigen; a preliminary communication. p. 164
Vol. 50, no. 1, Jan. 1956
CHEMICKÉ LISTY (Československá akademie věd. Chemický ústav)
Praha, Czech.

SOURCE: EAST EUROPEAN ACCESSIONS (EEAL) VOL 6 NO 4 April 1957

Journal, p. 1

Isolation of pure ascorbigen (Preliminary communication).
 Z. Procházka, V. Šanda, and F. Šorm (Čsl. akad. věd,
 Prague). Chem. Listy 50, 167-8 (1956). From cabbage
 concentrates (cf. C.A. 48, 4033f), a compd. was obtained
 by paper chromatography, countercurrent extn., or frac-
 tional crystn. having the formula $C_{11}H_{11}NO_7$, m. 80-0°;
 picrate, m. 129-30°. Reduction of this compd., ascorbigen
 (I), with $LiAlH_4$, gave small amts. of 3 β -indolylactic acid, and
 3 β -indolylpropane-1,2-diol; alk. hydrolysis gave a small amt.
 of β -indolylacetic acid. A partial formula is proposed for I.
 M. Hudlický

Sum 3

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František, Sorm

CZECHOSLOVAKIA/Organic Chemistry. Natural Substances E-3
and Their Synthetic Analogues.

Abs Jour: Ref Zhur - Khimiya, No. 8, 1957, 26971.

Author : Šorm, František, Horák, Milan.

Inst :

Title : Steroids. XXII. Preparation of 3-Keto-16 β -
oxyandrostene-4 and 3-Keto-16 ξ -oxy-16 ξ -methyl-
androstene-4.

Orig Pub: Chem. listy, 1956, 50, No. 2, 282 - 287; Sb.
chekhoslov. khim. rabot, 1956, 21, No. 4, 926 -
937.

Abstract: By the reduction of acetate of Δ^5 -androstenole-
3 β -one-16 (I), 3-acetate of Δ^5 -androstendiole-
3 β , 16 α (II) and 3-acetate of Δ^5 -androsten-
diole-3 β , 16 β (III) were obtained, and the cor-
responding dioles (IV) and (V) were obtained

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CZECHOSLOVAKIA/Organic Chemistry. Natural Substances E-3
and Their Synthetic Analogues.

Abs Jour: Ref Zhur - Khimiya, No. 8, 1957, 26971.

Ni, the obtained mixture of II and III is left to stay 24 hours with 10 ml of dioxane, 1.5 ml of C_6H_5COCl and 1.5 ml of pyridine. First VI is received by chromatographing the benzene solution with 100 g of Al_2O_3 , yield 7.6%, melting

point 201 to 202° (from alc.), $[\alpha]_D^{20} -57^\circ$ (c 2.08), after that VII is received, yield 34%,

melting point 137 to 138°, $[\alpha]_D^{20} -56.1^\circ$ (c 2.27). A mixture of II and III is obtained by boiling the mixture of 383 mg of I, 100 ml of absolute ether and 400 mg of $LiAlH_4$ for 2 hours, decomposition of the complex with diluted H_2SO_4 and evaporating the ether extract; the mixture

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CZECHOSLOVAKIA/Organic Chemistry. Natural Substances and Their Synthetic Analogues. E-3

Abs Jour: Ref Zhur - Khimiya, No. 8, 1957, 26971.

in alcohol is boiled 2 hours and IV is produced, yield 93%, melting point 221 to 222° (from acetone), $[\alpha]_D^{20}$ -63.2° (c 0.95 in alc.-chloroform); V is similarly obtained from VII, yield 98%, melting point 155 to 156° (from acetone), $[\alpha]_D^{20}$ -69.5 (c 1.73). 100 mg of IV is hydrogenated in CH_3COOH on PtO_2 , the substance is boiled 2 hours with NaOH in alcohol, and after neutralization, XII is extracted with ether, from which XIII is received by benzylation, yield 50%, melting

point 181 to 183° (from alc.), $[\alpha]_D^{20}$ +9.7° (c 2.57). The mixture of 1.2 g of VII, 0.73

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APPROVED FOR RELEASE: 08/25/2000

CIA-RDP86-00513R001652420015-5

CZECHOSLOVAKIA/Organic Chemistry. Natural Substances and Their Synthetic Analogues.

Abs Jour: Ref Zhur - Khimiya, No. 8, 1957, 26971.

equ. of NaOH and 368 ml of absolute CH_3OH is left staying at 20°, the substance is extracted with ether after neutralization, washed with HCl acid and KHCO_3 and chromatographed with Al_2O_3 , IX is washed out with ether, yield 82%,

melting point 153 to 154° (from CH_3OH), $[\alpha]_D^{20}$ -38.6° (c 1.92). VII is produced from VI in

the same way, yield 56%, $[\alpha]_D^{20}$ -62.7 (c 1.66). 20 ml of solvents are distilled off from the mixture of 500 mg of IX, 40 ml of toluene and 10 ml of cyclohexanone, 3 ml of 10%-ual solution of Al isopropylate in toluene are added, 15 ml more are distilled off in 2 hours' time, the

Card 6/8

and Their Synthetic Analogues.

Abs Jour: Ref Zhur - Khimiya, No. 8, 1957, 26971.

the same way as IX, Δ^4 -16 ξ -methylandrostenole-16 ξ -one-3 (XV) is received, yield 54%, melting point 165 to 166° (from benzene), $[\alpha]_D^{20} +81.5^\circ$ (c 2.39). The position of the double bond in X and XV was confirmed with ultraviolet spectra. All $[\alpha]_D$ -s were determined in CHCl_2 .

Card 8/8

Sorm, František

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Plant substances. V. Isolation of further crystalline compounds from wormwood. Vlastimil Herout, Ladislav Novotný, and František Sorm (Czech. Acad. Sci., Prague). *Chem. Listy* 56, 691-7 (1956); cf. C.A. 49, 13228i. — Chromatography of ligroine-ext. of *Artemisia absinthium* (loc. cit.) on neutral Al_2O_3 yielded cryst. compds. in the following sequence: a yellow lactone, $C_{15}H_{14}O_2$, m. 207° (from $CHCl_3$); (Me₂CH)₂O; hydroxyguaiulenolide, m. 133-5°; a compd., m. 156° (from EtOH), $[\alpha]_D^{25}$ 285°; a hydroxy lactone, $C_{15}H_{14}O_2$, m. 98° (dimorphic form m. 108°, $[\alpha]_D^{25}$ -14.0°); absinthin dehydrogenated to chamazulene; a keto lactone, $C_{15}H_{12}O_2$, m. 114°, $[\alpha]_D^{25}$ -277°, (semicarbazone m. 222°); a compd., m. 124°; a keto lactone, $C_{15}H_{12}O_2$, m. 172°. The extd. drug was then treated with 96% EtOH, cryst. quebrachitol was sepd., and the filtrate was chromatographed, yielding absinthin, anabsinthin, a compd. m. 63°, and a compd. m. 252° which gave an acetyl deriv., m. 252°. L. J. Urišnek

SOMI, F.

SOMI, F. Proteins. XIV. Specificity of pancreatic proteinases in the fission of clupein. p. 623. Vol 50, no. 4, Apr. 1957. CHEMOTEX LISTY. Praha, Czechoslovakia.

SOURCE: East European Accessions List (EEAL) Vol. 6, No. 4--April 1957

SOBK, F.

SOBK, F. Changes in the content of adenosinetriphosphate during
germination of the bean. p. 632. Vol. 50, no. 4, Apr. 1956.
CHEMICKÉ LISTY. Praha, Czechoslovakia.

SOURCE: East European Accessions List (EEAL) Vol. 6, No. 4—April 1957

SORM, FRANTISEK

Effect of aconitine on the metabolism of animal tissues in vitro. III. Changes in the metabolism of brain, liver, and kidney slices in the presence of aconitine, potassium ions, and 2,4-dinitrophenol. Zdrávka Heránková and František Sorm (Czech. Acad. Sci., Prague). Chem. Listy 56, 637-41 (1960); cf. C.A., 49, 5360g. — Aconitine (I) in concns. 0.031-7.75 $\times 10^{-4}$ M was incubated with slices and homogenates of brain cortex, kidney cortex, and liver of rat under various conditions. I stimulated considerably oxidation of glucose, pyruvate, and succinate (II) in brain tissue, but does not influence oxidation of succinate, α -ketoglutarate, and L-glutamate. I does not stimulate respiration of kidneys and liver but effects a respiratory wt. of these tissues by 60-70% caused by retention of unidentified cryst. substances. The effect of K^+ ions (0.0065 M KCl) on the respiration of brain slices differs from the effect of I only quantitatively, whereas in brain homogenates with II as substrate K^+ does not stimulate respiration and practically abolishes stimulation brought about by I. The influence of 2,4-dinitrophenol (III) on respiration is not specific for brain tissue and differs from that of I by the mode of its action. The effects of I and III do not seem to be analogous while the effects of I and K^+ ions seems to be related. It is suggested that I takes action in metabolic systems sensitive to O₂ tension (cf. Dickens, *Actualities Biochem.* 10, 140 (1947)).
L. J. Urbanek

František, Sorm

CZECHOSLOVAKIA/Organic Chemistry. Natural Substances E-3
and Their Synthetic Analogues.

Abs Jour: Ref Zhur - Khimiya, No. 8, 1957, 26972.

Author : Fajkoš, Jan, Šorm, František.

Inst :
Title : Steroids. XXIII. Preparation and Proof of
Configuration of Both Stereoisomer 3β -Oxy-16-
acetyl Derivatives of Androstane.

Orig Pub: Chem. listy, 1956, 50, No. 5, 791 - 799.

Abstract: The configuration of some 16-substitutions of
androstane was established. The solution of
 Δ^{16} -16-cyanandrostenole- 3β acetate in ani-
sole is added at 20° to the ether solution of
 CH_3MgBr , heated 5 hours up to 60° , and Δ^{16} -
16-acetylandrostenole- 3β (I) is received by
usual treatment, yield 76%, melting point 202

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CZECHOSLOVAKIA/Organic Chemistry. Natural Substances E-3
and Their Synthetic Analogues.

Abs Jour: Ref Zhur - Khimiya, No. 8, 1957, 26972.

to 203° (from CH_3OH and sublimation), $[\alpha]_D^{20}$
 $-46 \pm 1^\circ$ (c 3.18). acetate (II), yield 73%, mel-
ting point 144 to 145° (from alc.), $[\alpha]_D^{20}$ -57
 $\pm 1^\circ$ (c 2.12). 16β -acetylandrostanole- 3β (III)
is received by hydrogenation of I on 5% ual Pd/
 CaCO_3 in dioxane (of 1 mol of H_2), yield 70%,
melting point 143 to 145° (from CH_3OH), $[\alpha]_D^{20}$
 $-22 \pm 1^\circ$ (c 2.63); acetate (IV) melting point
 95 to 96° (from CH_3OH), $[\alpha]_D^{20}$ $-38 \pm 1^\circ$ (c 3.8);
IV is prepared also by hydrogenation of II. The
known androstandiole- $3\beta, 16\beta$ diacetate was pre-
pared by oxidation of IV with perbenzoic acid
in CHCl_3 (7 days in darkness), yield 52%, melting
point 105 to 107° (from alc.), $[\alpha]_D^{20}$ -11.2
 $\pm 1^\circ$ (c 2.32). The 16β -configuration of III

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CZECHOSLOVAKIA/Organic Chemistry. Natural Substances E-3
and Their Synthetic Analogues.

Abs Jour: Ref Zhur - Khimiya, No. 8, 1957, 26972.

in pyridine (20°, 24 hours) produces Δ^{16-16} -acetylandrostenone-3 (VII), yield 83%, melting point 169 to 170° (from benzene), $[\alpha]_D^{20} -21 \pm 1^\circ$ (c 2.19). Oxidation of III with CrO_3 in CH_3COOH (20°, 20 hours) resulted in 16-acetylandrostanone-3, yield 57%, melting point 175 to 177° (from benzene), $[\alpha]_D^{20} -12 \pm 1^\circ$ (c 2.06), which can be prepared also by hydrogenating VII with Pd/CaCO_3 in dioxane, yield 83%. Similarly, oxidation of V produces 16 α -acetylandrostanone-3, yield 41%, melting point 172 to 174° (from benzene), $[\alpha]_D^{20} +15 \pm 1^\circ$ (c 2.43). Acetate of VIII (IX) was received by acetylizing 3 β -oxyandrostanecarboxylic-(16 α) acid (VIII) with $(\text{CH}_3\text{CO})_2\text{O}$ in pyridine (16 hours, 20°), yield 85%,

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CZECHOSLOVAKIA/Organic Chemistry. Natural Substances E-3
and Their Synthetic Analogues.

Abs Jour: Ref Zhur - Khimiya, No. 8, 1957, 26972.

converted into chloroanhydride (XII) with SOCl_2 ,
melting point of unpurified XII - 165 to 175°. Not the expected IV, but V was received from the
reaction of XII with $\text{Cd}(\text{CH}_3)_2$. In view of the
fact that IX and XI, as well as the chloroan-
hydrides X and XII are different one from the
other, epimerization should take place at the
interaction of XII with $\text{Cd}(\text{CH}_3)_2$. Ether solu-
tion of X is added to ether solution of an
excessive amount of CH_2N_2 at -10° and left
staying 12 hours at 20° , acetate of 16 α -diazo-
acetylandrostanole-3 β (XIII) is obtained, yield
70%, melting point 160 to 161° (from benzene),
/ α /20D +31 \pm 1° (c 2.36). Acetate of 16 α -bromo-
acetylandrostanole-3 β (XIV) is received from

Card 6/8

SORM, #.

med ✓ 6-Azauracil, an antimetabolite of uracil and cytosine in *Escherichia coli*. Preliminary communication. F. Sorm and J. Škoda (Čsl. akad. věd, Prague). *Chem. Listy* 50, 827 (1956).—6-Azauracil (I) is a strong inhibitor of growth of *Escherichia coli* B. Concn. $4 \times 10^{-6} M$ and $8 \times 10^{-6} M$ caused 60 and 100% inhibition, resp. At lower concns. of I, elongation of cells occurs instead of partition. The inhibition caused by I is stopped by uracil and cytosine, but not by thymine and purine bases. Presence of amino acids and nucleic acid in concn. $3 \times 10^{-4} M$ has no effect on the inhibition of I at a concn. $2 \times 10^{-6} M$. H. H. H. H. H.

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F. SORM

✓ The biosynthesis of serine from glycine in higher plants.
M. Zelinková and F. Sorm (Čsl. akad. věd, Prague). *Chem. Listy* 50, 841-3 (1956). The biosynthesis of serine (I) from glycine (II) in higher plants takes place only *in vivo*, not in plant homogenates. Optimum concn. of II was 0.1M, applied by the method of vacuum infiltration at 27, 30, and 37° in seedlings of pea, barley, oat, rye, and wheat. The biosynthesis of I is inhibited by inhibitors of respiration (2 X 10⁻³M CN⁻, 10⁻³M A₂O₃). Carbon of II is held to be a precursor of the CH₂OH group. M. Hudlický

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SOHN, F.; KORNHUB, H.; HELD, V.

Terpense. LXXI. Helenalin, a further lactone of the guaianolide group. p. 985.
(Chemische Listy, Praha. Vol. 50, no. 6, June 1956.)

SO: Monthly List of East European Accession (EEAL) LC, Vol. 6, no. 7, July 1957. Uncl.

~~FRANTISEK~~ SORM, Frantisek

Steroids. XXIV. Structure of holarrhizin, Václav Cerný, Ludvík Lábl, and František Sorm (Českoslov. akad. věd, Prague). Chem. Listy 50, 1120-23 (1956); cf. C.A. 50, 15571c. — Deoxydihydrooctramethylholarrhizin (I) prepd. from 3 β ,20 α -bis(dimethylamino)-1 β -oxallopregnane (II) was found to be identical with 3 β ,20 α -bis(dimethylamino)-allopregnane (I) prepd. either from 2 β -acetoxybismorallolcholeic acid (III), or from 3 β -acetoxy-20-oxallopregnane (IV). Heating 250 mg. II with 550 mg. 80% $\text{NH}_4\text{H}_2\text{O}$, 8.5 ml. EtOH , and 240 mg. Na 32 hrs. at $200-10^\circ$ under N in a sealed tube, dilg. the mixt. with H_2O , extg. with Et_2O , and chromatographing the ext. in C_6H_6 soln. over 6 g. Al_2O_3 gave, by C_6H_6 elution, 90 mg. oil, from which was obtained 45 mg. cryst. I, m. $123-4^\circ$ (from Me_2CO), $[\alpha]_D^{25} 26^\circ$. The compd. is dimorphous; the other form, isolated from another expt., m. $100-8^\circ$, $[\alpha]_D^{24} 24^\circ$. It can be transformed to the first form by seeding the soln. in Me_2CO . Treating 4.23 g. IV, m. $142-4^\circ$, with 1 g. $\text{NH}_4\text{OH}\cdot\text{HCl}$ in 8 ml. pyridine, adding 17 ml. pyridine, allowing to stand overnight, dilg. the mixt. with H_2O , and extg. with Et_2O gave 4.25 g. oxime of IV, m. $195-7^\circ$, $[\alpha]_D^{15} 15^\circ$. Portionwise reduction of 5.97 g. IV oxime with 40 g. Na in 405 ml. EtOH at $105-10^\circ$ (45 min.), diln. of the mixt. with H_2O , steam-distn. of the EtOH , and ether extn. gave 4.55 g. crude amine which was heated 4 hrs. on the steam-bath with 24 ml. HCO_2H and 30 ml. 40% CH_3O . The soln. was dild. with 4 vols. of H_2O , filtered, alkalinized with NH_4OH , extd. with Et_2O and the ext. acetylated with 25 ml. Ac_2O and 60 ml. $\text{C}_6\text{H}_5\text{N}$ overnight at room temp. Alkalinization of the dil. soln. with NH_4OH , extn. with Et_2O , and chromatography over 120 g. Al_2O_3 yielded, by petr. ether elution, 20% 3 β -acetoxy-20 α -dimethylamino-*allopregnane* (Va), m. $161.5-2.5^\circ$ (from Me_2CO and Et_2O), $[\alpha]_D^{15} 1^\circ$, and (by petr. ether and benzene elution), 5% 3 β -acetoxy-20 α -dimethylamino-*allopregnane* (Vb), m. $159-60^\circ$ (from Et_2O and Me_2CO), $[\alpha]_D^{15} 12^\circ$. Refluxing 990 mg. Va with 110 mg. K_2CO_3 in 70 ml. MeOH , 5 ml. C_6H_6 , and 4 ml. H_2O 2 hrs., evapg. the mixt., dilg. with H_2O , and extg. with

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CERNY, VACLAV, LADOK, LUDVIK, ...

Et₂O gave 877 mg. 3 β -hydroxy-20 β -dimethylaminoallopregnane (VIa), m. 178.5-9° (from Me₂CO), [a]_D²⁵ 12.5°. Oxidation of 877 mg. VIa in 30 ml. AcOH with 300 mg. CrO₃ in 2 ml. H₂O at room temp. overnight, diln. of the mixt. with ice, alkalization with NH₄OH, and extn. with Et₂O gave 487 mg. 3-oxo-20 β -dimethylaminoallopregnane (VIIa), m. 159-60° (from Me₂CO), [a]_D²⁵ 34°. Allowing a mixt. of 660 mg. VIIa, 490 mg. NH₄OH.HCl, and 30 ml. C₂H₅N to stand overnight at room temp. 2 days, dilg. the mixt. with H₂O, alkalizing with NH₄OH, and extg. with Et₂O gave 280 mg. VIIa oxime, m. 240-4° (from EtOH). Adding in the course of 5 hrs. at 120° 1.25 g. Na to 255 mg. VIIa oxime in 18 ml. AmOH, dilg. the soln. with ice, acidifying with 2N H₂SO₄, steam distg. the AmOH, extg. the soln. with Et₂O, sepg. the Et₂O layer, evapg. the Et₂O dissolved in the aq. layer with steam, alkalizing the soln. with NH₄OH, extg. the base with Et₂O, evapg. the ext., heating the residue (260 mg.) 5 min. on the steam bath with 140 mg. p-O₂NC₆H₄CHO, decomp. the resulting crystals (218 mg.) by heating with 20 ml. 2N H₂SO₄, removing the p-O₂NC₆H₄CHO with Et₂O, alkalizing the aq. layer with NH₄OH, extg. the base with Et₂O, evapg. the ext., heating the residue (148 mg.) 4 hrs. at 100° with 4.5 ml. 40% CH₃O and 3.6 ml. HCO₂H, dilg. the mixt. with 4 vols. H₂O, filtering, alkalizing with NH₄OH, and extg. with Et₂O gave 90 mg. 28,20 β -bis(dimethylamino)allopregnane (VIII), m. 123.5-4.5° (from Me₂CO), [a]_D²⁵ +17°. Sapon. of Vb (247 mg.) with 33 mg. K₂CO₃ in 1 ml. H₂O and 16.5 ml. EtOH gave 180 mg. 3 β -hydroxy-20 α -dimethylaminoallopregnane (IX), m. 170-1.5°, [a]_D²⁵ 25.5°. The same product, m. 172°, [a]_D²⁵ 25°, was obtained from III as follows: treating 1 g. III, m. 193°, with 16 ml. SOCl₂, dissolving the crude chloride of III, m. 126-6°, in 24 ml. Me₂CO, adding a soln. of 600 mg. NaN₃ in 2.4 ml. H₂O with ice-cooling, dilg. the mixt. after 20 min. with 60 ml. ice-water,

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SERM, FRANTIŠEK

✓ Antagonism between 6-azauracil and some pyrimidine derivatives in *Escherichia coli*. Jan Škoda and František Šorm (Českoslov. akad. věd, Prague). *Chem. Listy* 50, 1105-8 (1956).—The growth of *E. coli*, *Salmonella typhimurium*, *S. paratyphi*, *Rhodotorula gracilis*, and *Penicillium roquefortii* is inhibited by 6-azauracil (I) in low concns. The inhibition is strictly competitive. The inhibition effects may be removed by uracil, cytosine, and uridine. The possible places of interference of I in the synthesis of nucleic acids in *E. coli* are suggested. M. Hudlický

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FORM FRANTISEK

Terpenes. LXXII. Preparation of pure compounds of the α - and β -santalane series Vlastimil Herout, Václav Janáček, and Josef Přibyl, Czech Acad. Sci., Prague

considerably purer α -santalene (I) and β -santalene (II) than those described by Guba, *et al.* (C.A. 40, 5030¹). I $[\alpha]_D^{25}$ 12.5°, d_4^{25} 0.9075, n_D^{25} 1.4877, II $[\alpha]_D^{25}$ -92.5°, d_4^{25} 0.8930, n_D^{25} 1.4930. The mixt. of α -santalol (III) and β -santalol (IV) obtained via acid phthalic esters was sepd. by distn. to give III, b_p 129°, $[\alpha]_D^{25}$ 17.9°, d_4^{25} 0.9769, n_D^{25} 1.5023, and IV, b_p 133°, $[\alpha]_D^{25}$ -90.5°, d_4^{25} 0.9750, n_D^{25} 1.5115. I and II were hydrogenated on PtO₂ in AcOH to give α -santalane (V), $[\alpha]_D^{25}$ 5.3°, d_4^{25} 0.8896, n_D^{25} 1.4753 and β -santalane (VI), $[\alpha]_D^{25}$ 4.6°, d_4^{25} 0.8712, n_D^{25} 1.4712, resp. Hydrogenation of III followed by chromatography on Al₂O₃ gave *dihydro- α -santalol* $[\alpha]_D^{25}$ 4.4°, d_4^{25} 0.9712, n_D^{25} 0.4873 besides V with slightly different properties $[\alpha]_D^{25}$ 9.1°, d_4^{25} 0.8806, n_D^{25} 1.4650. Analogous treatment of IV yielded *tetrahydro- β -santalol*, $[\alpha]_D^{25}$ 4.4°, d_4^{25} 0.9574, n_D^{25} 1.4918 besides VI, $[\alpha]_D^{25}$ 0.3°, d_4^{25} 0.8680, n_D^{25} 1.4687. Infrared spectra of all compds. were evaluated and discussed. LXXIII. *Cis- and trans-bicyclo[0.3.5]decane*. František Šorm and Miroslav Romanuk. *Ibid.* 1277-81. ~~Chemical~~ aspects were studied of

hydrogenation of the bicyclo[0.3.5]decane series deriva. possessing a double bond between the rings. Addn. of 300 mg. BF₃·Et₂O to a mixt. of 185 mg. *cis*-bicyclo[0.3.5]decane-4-one (I) (cf. Šorm, C.A. 41, 4140A) and 200 mg. (CH₃SH)₂ under cooling, followed by homogenization with 4 ml AcOH, treatment of the reaction mixt. with excess aq. soln. of K₂CO₃, extrn. with Et₂O and distn., gave 270 mg. *ethylenethioketal* of I; this was desulfurized by boiling with Raney-Ni in dioxane, poured into H₂O and extrd. with ligroine to give, on distn., 128 mg. *cis*-bicyclo[0.3.5]decane (II), d_4^{25} 0.8823, n_D^{25} 1.4761. Similarly *trans*-bicyclo[0.3.5]-

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HEROUT, Vlastimil; JAROLÍM, Vlastimil; PLEŠA, Josef...
 decane-1-one was converted to *trans*-II, d_n 0.8794, n_D^{20} 1.4761. Bicyclo[0.3.5]deca-1(7).2-diene (III), prepd. from 1,2,3,4,5,6,7,8-octahydronaphthalene, b_p 75°, d_n 0.9395, n_D^{20} 1.5257. Catalytic hydrogenation of III by 3 alternative methods (PtO₂, Raney-Ni, and Pd-C) yielded in each case practically pure *cis*-II. Likewise, hydrogenation (PtO₂) of azulene which was obtained by catalytic dehydrogenation of III, yielded *cis*-II. On the basis of infrared-spectra and physico-chem. properties of these compds. the authors conclude that hydrogenation of the bicyclo[0.3.5]deca type hydrocarbons gives rise solely to *cis*-annulation. This finding is in agreement with the assumptions of Kovats, *et al.* (C.A. 48, 10053c) concerning the stereospecific course of hydrogenation of bicyclic decenes under pressure. LXXIV. Junenol, a new sesquiterpenic alcohol from juniper oil. Otake, Mott, Vlastimil Herout, and František Šorm. *Ibid.* 1282-8; cf. C.A. 49, 4585d. —The constitution of 3-cryst. C₁₅H₂₆O alic. (I) isolated from juniper oil by distn. and chromatography on Al₂O₃ was studied. Alc. b_p 123-5°, m . 139-40° (Ia) was shown to belong to the eudesmane type, while alc. b_p 134-5°, m . 106.5° (Ib) called "juniper camphor" was of the selinane type, alc. b_p 121-2°, m . 62.5-3° (Ic) designated as junenol had the structure of 10-methyl-1-methylene-7-isopropyl-8-decalol[phenylurethan, m . 180.5° (from ligroine), $[\alpha]_D^{25}$ -40.8° (in CHCl₃); α -naphthylurethane, m . 189° (from ligroine), $[\alpha]_D^{25}$ -32.5° (in CHCl₃)]. Ic was hydrogenated with PtO₂ in AcOH to a satd. alc. C₁₅H₂₆O (II), m . 115.5° (from ligroine), $[\alpha]_D^{25}$ \pm 0°. II was dehydrated by heating to 180° with KHSO₄ to give a mixt. of hydrocarbons which on hydrogenation yielded selinane. Oxidation of Ic with KMnO₄ or OsO₄ gave triol C₁₅H₂₆O₃ (III), m . 133° (from ligroine-C₆H₆), $[\alpha]_D^{25}$ -37.3° (in EtOH). Ozonization of Ic in CH₂Cl₂ at -30° followed by chromatography on Al₂O₃ gave HCOH and hydroxyketone C₁₅H₂₄O₂ (IV), m . 45.5° (from ligroine), $[\alpha]_D^{25}$ 11.9°; semicarbazone, m . 212-13° (decomp.). IV was also obtained by oxidizing III with HIO₄ in EtOH. IV was

HEROUT, VLASTMIL; JAROLIM, VACLAV; PLIVA, JOSEF.
oxidized with NaOH in dioxane at 60° to give compd. C₁₈H₂₀O₄, m. 189° (from EtOH). Oxidation of II with CrO₃ in AcOH at 20° yielded ketone C₁₈H₂₀O (V), m. 84.5°, [α]_D²⁰ 5.8° (in EtOH); treatment of V with Br in AcOH at 40° gave a derivative, C₁₈H₂₀OBr₂, m. 105° (from EtO). Dehydration of Ia by heating under reflux to 100° with a trace of iodine gave rise to a liquid mixt. of dienes C₁₈H₂₀. d₄ 0.9166, n_D²⁰ 1.5228, [α]_D²⁰ 265.3°, the absorption spectrum of which shows the presence of 2 double bonds. LXXV.
Cis- and trans-homocaryophyllenic acids. Václav Jarolim, Milan Streibl, Ladislav Dolejš, and František Šorm. *JACS*, 123(1901); cf. Elsevier's Encyclopaedia of Org. Chemistry, 12A, 71-2(1948).—The synthesis of homocaryophyllenic acid (I) and its relationship to some terpenic compounds was studied with special consideration of the configuration I di-Me ester. Di-I, m.p. 63.2°, d₄ 0.946, n_D²⁰ 1.4408, was obtained by acid saponification of the unstable diester Ia, m.p. 42° which was prepared as a trans configuration. The diester Ia, m.p. 42° was prepared from the ketone C₁₈H₂₀O (V) and the diene C₁₈H₂₀ by heating with AlCl₃ at 220°. Ia was saponified with KOH and the resulting mixture was neutralized with HCl. Ia was partially converted to di-I, m.p. 63.2°, from methyl vinylcarbazate. Saponification of di-I with KOH, EtOH, and Me₂S gave the diester Ia, m.p. 42°. Ia was heated from 136° to 155° at 0.5 mm. pressure and 155° at 0.1 mm. pressure to give di-I, m.p. 63.2°, which was purified by reprecipitation from ethyl acetate. Ia, m.p. 42°, which was heated by treating to 45° with acetic Mercuric chloride, the resulting intermediate inverted with SOCl₂ to ester-chloride of cis-II, b.p. 3.3°, and treated with CH₃N₃ in Et₂O to yield about 3 g. di-Me ester of cis-II. An economical method has been found out for the preparation of Ia starting from the Me ester of the ketone and C₁₈H₂₀O (III) which is the most suitable isomerization of caryophyllene. A solution of 4 g. of III in 50 ml. Et₂O was added dropwise at -5° to 150 ml. Br₂, the mixt. adjusted to pH 8.4, and under vigorous stirring and cooling to -5 to 0° 8 g. of III added and the reaction mixt. left overnight.

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HEROUT, Václav; JAROLÍN, Václav; PLIVA, Josef, .
 After addn. of Na_2SO_4 the mixt. was acidified with H_2SO_4 and extd. with 5 l. Et_2O . The extd. material was esterified with MeOH-HCl and the esters (101 g.) sepd. by distn. in vacuo to yield 30 g. $\text{CHBr}_3\text{CO}_2\text{Me}$, 10.5 g. *trans*-II, and 32.0 g. di-Me ester of *trans*-I. The synthesis of I from *trans*-II according to Dawson and Ramage (*C.A.* 46, 8068a) was revised. Contrary to their findings the chief product was *trans*-I and in addn. there was also obtained *trans*-3,3-dimethylcyclobutane-1,2-diacetic acid, m. 101-2° ($\text{C}_{10}\text{H}_{16}\text{O}_4$ ligroine) characterized as di-Me ester, b_p 135°, d₄ 1.0297, n_D 1.4472; dianilide, m. 170-1° (from KtOH); di-p-toluide, m. 183° (from EtOH). LXXVI. Synthesis of caryophyllene: chemical proof of the carbon skeleton of caryophyllene. Václav Jarolín, Milan Streibl, Ladislav Dolejš, and František Šorm. *Ibid.* 1299-303.—Proof is given for the structure of caryophyllene with trans-annulation. *trans*-Homocaryophyllenic dichloride (Ia) was obtained in 14.5-g. yield from 20 ml. SOCl_2 with 12 g. acid at 40°. Ia (3.7 g.) in Et_2O was added dropwise at -20° under vigorous stirring to 4.5 g. EtN_3 in Et_2O , the mixt. allowed to reach room temp. and the solvent evapd. at about 10°. The resulting diazoketone was dissolved in a mixt. of 20 ml. PhCl_3OH and 17 ml. collidine and the rearrangement carried out immersing the flask for 5 min. into a paraffin bath heated to 180-90°, to yield, after sapon. by boiling 3 hrs. with 10% MeOH-KOH , 2.4 g. crude α -methyl- γ -(2,2-dimethyl-4-(α -carboxy)ethyl)cyclobutylbutyric acid (I); 22 g. I was esterified to give, on distn., 18.7 g. di-Me ester of I, b_p 127°, d₄ 0.8867, n_D 1.4535, M_R 77.7. The di-Me ester (15.1 g.) was dissolved in 160 ml. MeOH -soln. of 4.57 g. Ba(OH)_2 , kept overnight and the MeOH distd. off below 45°. After extg. the nonreacted material with Et_2O the soln. was acidified with HCl to pH 5.5 and shaken with 150 ml. Et_2O to yield, on distn., 5.2 g. mixt. of semiesters of I, b_p 133-42°. After converting the semiesters to ester chlorides of I by means of SOCl_2 , the mixt. (10.5 g.) was treated with 4.5 g.

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HERBUT, VLADIMIR; JABLON, VACLAV; PLYVA, JOSEF...

CH_2N_2 yielding, on esterification, 5.0 g. mixt., b_p 175-80° of di-Me β -methyl-3-[3,2-dimethyl-4-(α -carboxy)ethyl]cyclobutylvalerate (II) and di-Me α -methyl- γ -[3,2-dimethyl-4-(α -methyl- β -carboxy)ethyl]cyclobutylbutyrate (III). A mixt. of

II and III (5.0 g.) was subjected to acyloin cyclization with 2 g. powdered Na in 600 ml. boiling xylene to give, after decmpn. with dil. H_2SO_4 , 2.1 g. fraction b_p 95-100° consisting of 4,8,11,11-tetramethylbicyclo[0,2,7]undecane-5-ol-6-one and 4,8,11,11-tetramethylbicyclo[0,2,7]undecane-6-ol-7-one. The acyloin fraction (1.0 g.) was reduced by boiling with 10.5 g. Zn-Hg in 40 ml. AcOH and 35 ml. concd. HCl which was added gradually during 60 hrs. The reaction mixt. was dild. with H_2O , extd. with ligroine and chromatographed on 80 g. alk. Al_2O_3 to give 350 mg. ketonic fraction, apparently of 4,8,11,11-tetramethylbicyclo[0,2,7]undecane-(1)-one (semicarbazone, m. 190° from EtOH) and 950 mg. hydrocarbon fraction which was hydrogenated (406 mg.) on PtO_2 in AcOH and the product purified on silica gel to yield 396 mg. 4,8,11,11-tetramethylbicyclo[0,2,7]undecane (IV), b_p 130-2°, d_m 0.8705, n_D^{20} 1.4769, M_R 67.65. The identity of IV with caryophyllane obtained from natural sources by hydrogenation was proved by infrared spectra and physico-chem. consts.

L. J. Urbánek

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Jan. 19, 1957, 1958

Terpenes. LXXVI. The nature of arctiopicrin, an unsaturated lactone from *Arctium minus*. ~~Arctium minus~~ Vlastimil Horout, and František Štoll (Czechoslovakia, Prague). *Chem. Zvesti* 53, 1957-224 (1956); cf. C.A. 51, 2972. A lactone, arctiopicrin, (I), isolated from *A. minus*, has the formula $C_{11}H_{16}O_3$, contrary to the previous formulation as $C_{11}H_{14}O_3$. Hydrogenation of I yielded two stereoisomers (II and III), $C_{11}H_{18}O_3$, and two stereoisomers (IV and V), $C_{11}H_{16}O_4$. The main product of hydrogenation, IV, yielded on hydrolysis $Me-CH(CH_2OH)CO_2H$ (VI) and a monocyclic diol-lactone (VII) called *arctidiolide* ($C_{11}H_{16}O_4$). I, m. 115°, $[\alpha]_D^{25}$ 133°, was obtained in a yield of 0.05% from dried leaves of *A. minus*. I in alk. hydrolysis consumed 2.10 equivs. base. Hydrogenation of 5.1 g. I in 30 ml. MeOH over PtO_2 (equiv. of 2.35 double bonds), chromatography over 5 kg. Al_2O_3 , and crystn. from 10:1 iso-PrOH-EtOH gave 200 mg. II, m. 93°, $[\alpha]_D^{25}$ -6.2°, 1.15 g. III, m. 108°, $[\alpha]_D^{25}$ -21.7° (*phenylurethane*, m. 134°), 1.63 g. IV, m. 134°, $[\alpha]_D^{25}$ 52.48° [*bis(phenylurethane)*, m. 149°, *diacetate*, m. 53°], and 550 mg. V, m. 118°, $[\alpha]_D^{25}$ 79.7°. Refluxing IV (1.2 g.) with 20 ml. 10% KOH in MeOH, neutralizing the cold mixt. with a calcd. amt. of HCl in MeOH, treating it with CH_3N in Et_2O , filtering off the KCl, and distg. the filtrate gave 210 mg. VI *Me ester*, b.p. 74°, $[\alpha]_D^{25}$ 6.4°, reduction of which with LiAlH₄ in Et_2O gave $HOCH_2-CHMe-CH_2OH$, b.p. 140° [*bis(phenylurethane)*, m. 127°]. VI and its transformation products were identified with those prepd. synthetically. The residue after the removal of VI *Me ester* yielded *tetrahydroarctidiolide*, m. 145° [from $EtOH-(iso-Pr)_2O$] b.p. 176°, $[\alpha]_D^{25}$ 55°. Infrared spectra of I-V are given. M. Hudlický

SORM, FRANTISEK.

✓ Organosilicon compounds. XI. Material balance of the direct synthesis of methylchlorosilanes. Karel Sedláček, Vladimír Bafant, and František Sorm (Czech. Acad. Sci., Prague). Chem. Listy 50, 1954-5 (1956); cf. C.A. 51, 4208f. The app. is described and the amts. and ratios are given of the products obtained by treatment of an alloy contg. Si 86.50, Cu 9.73, Fe 1.84, Al 0.13, and Mg 0.16% (size of granules 0.1-0.3 mm.) with dry MeCl. This reaction yields Me₂SiCl₂, MeSiCl₃, Me₂SiCl, MeSiCl₂, MeSiHCl₂, SiHCl₃, H₂, CH₄, C₂H₆, and C₃H₈, besides a small fraction, b. 8°, contg. SiH₃Cl and MeSiH₂Cl. A table and 18 graphs show the degree of methylation of Si in dependence on 2 variables, temp. (I) and flow rate (II) of MeCl, other conditions being const. Lowest I approaching 300° favor formation of highly methylated chlorosilanes. Formation of hydrocarbons is enhanced with raised I and diminished with increased II. The influence of raised I on the yield of methylchlorosilanes is compensated by increasing II, whereas formation of hydrocarbons and of H is effected solely by I. L. L. Urbánek

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✓ Effect of aconitine on the metabolism of animal tissues in vitro. III. Effect of aconitine and potassium ions on aerobic glycolysis in the brain cortex. Zdeňka Beránková and František Šorin (Czech. Acad. Sci., Prague). *Chem. Listy* 50, 2018-21 (1956); cf. *C.A.* 50, 9624c. Aconitine (I) stimulates O consumption and formation of lactic acid (II) in slices of rat-brain cortex. Max. increase in II-formation (by as much as 300%) produced by 50 mg. % I is observed during the 1st hr., i.e. in the phase when there is still a stimulation of respiration. I exerts a similar but considerably weaker effect in homogenates of brain cortex (150% approx.). Formation of II is enhanced in slices but slightly lowered in homogenates by K ions. The considerable increase of II-formation in slices caused by I in concn. 50 mg. % is lowered to half by the presence of K ions whereas effect of 0.1 mg. % I is not influenced by increased aunts. of K ions. In homogenates K ions suppress entirely stimulation of II formation brought about by I. Authors suggest that in the presence of I there is an increased H transfer by means of coenzyme I and explain the influence of K ions on the effect of I as a stabilizing influence of K ions and by interaction between I and K ions. I. J. Ucháček

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Med

Antibacterial action of ethyl ester of diazopyruvic acid
and its antagonism with leucine (isoleucine) in *Escherichia*
coli. F. Šorm and J. Škoda (Chem. Inst., Acad. Sci.
Czech. Prague). *Doklady Akad. Nauk S.S.S.R.* 107,
291-4 (1956).—Growth curves of *E. coli* in contact with Et
diazopyruvate in the nutrient medium are shown. The
ester causes at low concns. a growth of the organism in
fibrous cellular form. Total protein hydrolyzate added to
the nutrient blocks this effect of the ester. At all concns.
the ester represses the development of *E. coli*. The repress-
ing action depends on antagonism with leucine and iso-
leucine, and to lesser degree with aspartic acid, methionine,
serine, and valine. Synergistic effect of the ester in com-
bination with common antibiotics (penicillin, streptomycin,
Aureomycin, Terramycin, and chloramphenicol) was estab-
lished, with max. effect obtained from penicillin.

G. M. Kosolapoff

med. 2

SABLIK, Jaromir; SOCH, Frantisek

Antitumorous action of 6-azauracil on some transplantable experimental tumours. Neoplasma, Bratisl. 4 no.2:113-118 1957.

1. Pathophysiological Department, Oncological Institute, Praha,
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Science, Praha. Address: Akademik P. Sern, Praha 19, Na civicisti 2.

(NEOPLASMS, exper.

eff. of 6-azauridine on transplantable neoplasms)

(NUCLEOTIDES, eff.

6-azauridine on transplantable exper. neoplasms)

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KEILOVA, Helena; SORM, Frantisek

Potentiation of the antitumorous action of 6-azauracil by procaine
and excretion of 6-azauracil from the body. Neoplasma, Bratisl.
4 no.3:204-207 1957.

(URACIL, antag.

6-azauracil, potentiation of antitumorous action
by procaine & excretion in mice)

(CYTOTOXIC DRUGS, eff.

same)

(NEOPLASMS, exper.

eff. of 6-azauracil, potentiation of antitumorous
action by procaine & excretion in mice)

CZECHOSLOVAKIA/Organic Chemistry. Naturally Occurring
Substances and Their Synthetic Analogs.

G-3

Abs Jour: Ref Zhur-Khim., No 13, 1958, 43485.

Author : Schwarz Vladimir, Cerny Vaclav, Sorn Eratisek.

Inst :

Title : On Steroids. XXX. Preparation of 3 β -Acetoxy-16 α -Hydroxy-Allo-Ethianic Acid.

Orig Pub: Chem. listy, 1957, No 7, 1362-1366.

Abstract: Description of the synthesis of 3 α -acetoxy-16 α -hydroxy-allo-ethianic acid (I), starting from $\Delta^{5,16}$ -pregnadienol-3 β -one-20, by consecutive epoxydation, reduction, introduction of OH-group in position 21, and oxidation with HIO_4 . By hydrogenation of $\Delta^{5,16}$ -16 α , 17 α -epoxypregnenol-3 β -one-20 in alcohol and dioxane over Pd/CaCO_3 , and

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Abs Jour: Ref Zhur-Khim., No 13, 1958, 43485.

in C_5H_8N -- the acetate of III, yield 91%, MP 173-174°, $[α]_D^{25} +25°$ (c 2.2; chloroform). II is brominated by action of Br_2 in CCl_4-CH_3COOH mixture, in presence of HBr (gas), at 20°, the unpurified bromide is allowed to stand with NaI in C_6H_6 and alcohol for 36 hours and the product of the reaction is boiled 7 hours in acetone with CH_3COOK , to get the diacetate of 16 $α$, 17 $α$ -epoxy-allo-pregnandiol-3, 21-one-20, yield 80%, MP 149-150°. By reduction of the latter with $Cr(CH_3COO)_3$, analogously to reduction of II, is obtained the 3,21-diacetate of allo-pregnandiol-3, 16 $α$, 21-one-20 (IV), yield 34%, MP 169-170° (from benzene), $[α]_D^{25} +58.5°$ (c 1.7; chloroform); acetate, MP 160-161° (from CH_3OH), $[α]_D^{25} +44°$.

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